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THE NITRITE-ACCELERATED PHOTOCHEMICAL DEGRADATION OF CELLULOSE AS A PRETREATMENT FOR MICROBIOLOGICAL CONVERSION TO PROTEIN

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In an attempt to solve the problems involved in solid waste management, this study examines the conversion of waste cellulose to protein. This report, published by the National Environmental Research Center - Cincinnati, investigates the feasibility of using nitrite-accelerated photodegradation as a pretreatment for waste cellulose before converting the cellulose to protein.

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Director
National Environmental
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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	
ABSTRACT	1
SUMMARY AND CONCLUSIONS	4
I. INTRODUCTION	8
II. BACKGROUND INFORMATION	10
III. EXPERIMENTAL	17
IV. RESULTS AND DISCUSSION	18
A. Actinometry of the reactor	18
B. Irradiation of dry cotton linters paper	18
C. Cellulose suspensions	22
1. Cotton linters paper	22
2. Wood pulp cellulose	23
V. REFERENCES	43
APPENDIX - MATERIALS AND METHODS	47
A. Materials	47
1. Substrates	47
2. Chemicals and Reagents	47
3. Equipment	48
B. Methods	50
1. Treatment of Substrates with Soluble Salts	50
2. Ultraviolet Irradiation	51
3. Determination of Degree of Polymerization	51
4. Actinometry	52
5. Determination of Nitrite	53
6. Determination of Accessibility to Water	53

LIST OF TABLES

Table No.	Title	Page
1	Radiation Intensities in the Rayonet Reactor	56
2	Degree of Polymerization of SW-40 Solka-Floc Slurries in Sodium Nitrite Solutions After Irradiation at 254 NM.	57
3	Degree of Polymerization of SW-40 and BW-200 Solka-Floc Slurries in Dilute Sodium Nitrite Solutions After Irradiation for 19 Hours at 254 NM.	58

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LIST OF TABLES (Continued)

Table No.	Title	Page
4	Degree of Polymerization of BW-200 Solka-Floc Irradiated for Various Times at 254 NM as 10 Percent Slurries in Dilute Sodium Nitrite Solutions	59
5	Effect of Slurry Concentration of BW-200 Solka-Floc in Dilute Sodium Nitrite Solutions Upon Degree of Polymerization Following 19 Hours' Irradiation at 254 NM	60
6	Effect of Wavelength on the Degree of Polymerization of 2.7 Percent Slurries of SW-40 Solka-Floc in Sodium Nitrite Solutions Irradiated for 19 Hours	61
7	pH of Filtrates from the Irradiation of 1.5 Percent Slurries of SW-40 Solka-Floc in Sodium Nitrite Solutions at 254 NM	62
8	pH of Solka-Floc Slurries to Which 1N Sulfuric Acid was Added	63
9	pH of Filtrates from Solka-Floc Slurries Which had Little or no Irradiation	64
10	Irradiation of Solka-Floc Slurries to Which Various Amounts of 1N Sulfuric Acid or 1N Sodium Hydroxide had been Added	65
11	Irradiation of 10 Percent BW-200 Solka-Floc Slurries in 1 Percent Sodium Nitrite, with and without Added 1N Sulfuric Acid, in Oxygen or Nitrogen Atmospheres.	66
12	Irradiation of 0.25 Percent Sodium Nitrite Solution in Water with 254 NM Radiation	67
13	Analysis for Nitrite of Filtrates from Irradiated Slurries with Various Additives and Atmospheres.	68
14	Absorption at Selected Wavelengths of Filtrates from 2.7 Percent SW-40 Solka-Floc Slurries Following Irradiation for 19 Hours.	69
15	Apparent Quantum Efficiencies in the Irradiation at 254 NM of Cotton Linters Paper Strips with 1 Percent Sodium Nitrite Add-on.	70
16	Apparent Quantum Efficiencies in the Irradiation at 254 NM of SW-40 Solka-Floc Slurries in 1 Percent Sodium Nitrite Solutions	71
17	Apparent Quantum Efficiencies in the Irradiation at 254 NM of 2.7 Percent Slurries of BW-200 Solka-Floc in 1 Percent Sodium Nitrite Solutions.	72
18	Apparent Quantum Efficiencies in the Irradiation at 254 NM of 10 Percent Slurries of BW-200 Solka-Floc in Sodium Nitrite Solutions of Various Concentrations	73

LIST OF TABLES (Concluded)

Table No.	Title	Page
19	Accessibility to Aqueous Reagents of Several Cellulosic Materials as Determined by Hydrogen-Deuterium Exchange in Liquid Deuterium Oxide.	74
20	Yield of Bacteria Using Filter Cakes from Ultraviolet-Irradiated BW-200 Solka-Floc Slurries as the Carbon Source.	75
21	Yield of Bacteria Using Filter Cakes from Ultraviolet-Irradiated Solka-Floc Slurries as the Carbon Source . . .	76
22	Yield of Bacteria Using Ultraviolet-Irradiated Solka-Floc Slurries as the Carbon Source	77

LIST OF FIGURES

Figure No.	Title	
1	Effect of ultraviolet irradiation of various wavelengths on the degree of polymerization of untreated cotton linters paper	78
2	Effect of ultraviolet irradiation of various wavelengths on the degree of polymerization of sodium nitrite treated cotton linters paper.	79
3	Effect of 254 nm radiation on sodium nitrite treated cotton linters paper	80
4	Effect of 254 nm radiation on the number of scissions per molecule for sodium nitrite treated cotton linters paper. .	81
5	Depletion of sodium nitrite during irradiation of cotton linters paper originally containing 1% sodium nitrite . . .	82
6	Effect of 254 nm irradiation on the degree of polymerization of ferric chloride treated cotton linters paper..	83
7	Effect of wavelength on the degree of polymerization of irradiated cotton linters paper containing 1% ferric chloride.	84
8	Photomicrograph of SW-40 Solka-floc; transmitted light. . . .	85
9	Photomicrograph of BW-200 Solka-floc; transmitted light . . .	86
10	Effect of $NaNO_2$ concentration on the depolymerization of BW-40 Solka-floc slurries irradiated with 254 nm radiation	87
11	Photomicrograph of ball-milled BW-200 Solka-floc; transmitted light	88

LIST OF FIGURES (Concluded)

Figure No.	Title	Page
12	Photochemical reactor and "merry-go-round" sample holder. In the illustration the sample holder is loaded with paper strips, ready for irradiation. A quartz reaction tube, clamped to a support, is seen extending from the top of the reactor	89
13	Interior of the photochemical reactor showing the bank of lamps and the magnetic stirrer.	90
14	Calibration curve for the analysis of the actinometer solution.	91
15	Calibration curve for nitrite analysis.	92
16	Calibration curve for water accessibility determination . .	93

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We also wish to express our appreciation to Dr. Charles Dunlap of the Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana, for carrying out the bacterial growth experiments.

ABSTRACT

The feasibility of using nitrite-accelerated photodegradation as a pretreatment for waste cellulose prior to conversion to protein was investigated. The substrates used were cotton linters paper and purified wood cellulose.

Irradiation of the paper using ultraviolet sources with nominal peak intensities of 254 nm, 300 nm, and 350 nm, resulted in a gradual reduction of the degree of polymerization (DP), from an initial value of 1200. The shorter the wavelength, the more rapid the reduction in DP but, in all cases, the rate fell as the irradiation progressed. Irradiation of paper treated with sodium nitrite (1 percent add-on) resulted in a lowering of DP to about 300 in one hour and to about 225 in 24 hours. The changes in DP were independent of the wavelength. Further experiments with nitrite add-ons of 0.1 and 10 percent showed the rate of degradation to increase with nitrite content but less than proportionately above 1 percent. The nitrite content decreased during irradiation.

Irradiation of slurries of cellulose in aqueous solutions showed sodium nitrite to be effective in accelerating the degradation. The optimum concentration of sodium nitrite in solution was about 1 percent. In general, the shorter the wavelength, the greater the reduction in DP. The pH of the slurries generally fell as the irradiation progressed. The reduction in DP was greater if, in addition to sodium nitrite, the slurry

contained about 0.1 percent sulfuric acid. With sulfuric acid, the reduction in DP was slightly greater in an atmosphere of still air rather than in bubbling oxygen and considerably greater than in bubbling nitrogen. Cellulose slurries lost nitrite ion during irradiation. The greatest losses occurred in slurries which were acidified to about pH 4.

For short irradiations the apparent quantum efficiencies for lowering the DP of the dry papers exceeded those for the slurries, but for longer irradiations, the apparent efficiencies were higher for the slurries. The efficiencies were all less than 0.01 scissions/quantum.

Fungal growth tests using Aspergillus fumigatus did not show significant benefits in increased protein yields from any of the treated celluloses. However, bacterial growth tests using a mixed culture, Alcaligenes faecalis-Cellulomonas, sp., showed the rate of production of protein from certain of the photochemically-treated celluloses to be significantly enhanced. Since the effects could not be attributed to lowering of DP, it was concluded that chemical changes in the cellulose were probably important. In other experiments, without irradiation, it was found that even better results were obtained from samples which had been treated with 10 percent sodium hydroxide, or from samples which had been ball-milled to a small particle size.

While some of the photochemical pretreatments showed beneficial effects in accelerating bacterial protein production, the quantum efficiencies did not appear to be sufficiently high to be of practical

value for treatment of cellulosic wastes. However, it is possible that significant benefits could be obtained by less costly chemical treatments as well as by alkali swelling or by ball milling.

SUMMARY AND CONCLUSIONS

The feasibility of using nitrite-accelerated photodegradation as a pretreatment for waste cellulose prior to conversion to protein was investigated. The substrates used were cotton linters paper and purified wood cellulose. The method employed was to irradiate the dry paper, or a slurry of the cellulose in an aqueous solution, with ultraviolet light from lamps with nominal peak intensities of 254, 300 and 350 nm. In the case of the paper, this was usually treated so as to give add-ons of 0.1, 1 or 10% sodium nitrite prior to irradiation. Also the aqueous solutions used in making the slurries usually contained 0.1, 1 or 10% sodium nitrite, sometimes with a small quantity of sulfuric acid or sodium hydroxide. The indicated cellulose materials were irradiated for selected time intervals and the average degree of polymerization (DP) and hence, degree of degradation, determined from their intrinsic viscosities in cadoxene solutions.

Irradiation of the paper with any of the three wavelengths resulted in a gradual reduction in DP from an initial value of 1200. The shorter the wavelength, the more rapid the reduction in DP but, in all cases, the rate fell as the irradiation progressed. Irradiation of paper with a 1% add-on of sodium nitrite resulted in a lowering of DP to about 300 in one hour and to about 225 in 24 hours. The changes in DP were independent of the wavelength. Further experiments with nitrite add-ons of 0.1 and 10 percent showed the rate of degradation to increase with nitrite content but less than proportionately above 1 percent. The nitrite content decreased during irradiation.

Irradiation of slurries of cellulose in aqueous solutions showed sodium nitrite to be effective in accelerating the degradation. The optimum concentration of sodium nitrite in solution was about 1 percent. In general, the shorter the wavelength, the greater the reduction in DP. The pH of the slurries generally fell as the irradiation progressed. The reduction in DP was greater if, in addition to sodium nitrite, the slurry contained about 0.1 percent sulfuric acid. With sulfuric acid, the reduction in DP was slightly greater in an atmosphere of still air rather than in bubbling oxygen and considerably greater than in bubbling nitrogen. Cellulose slurries lost nitrite ion during irradiation. The greatest losses occurred in slurries which were acidified to about pH 4.

For short irradiations the apparent quantum efficiencies for lowering the DP of the dry papers exceeded those for the slurries, but for longer irradiations, the apparent efficiencies were higher for the slurries. The efficiencies were all less than 0.01 scissions/quantum.

Fungal growth tests using Aspergillus fumigatus were performed on the treated celluloses at the EPA Laboratories. None showed significant benefits in increased protein yields. However, bacterial growth tests carried out at Louisiana State University using a mixed culture, Alcaligenes faecalis-Cellulomonas, sp., showed the rate of production of protein from certain of the photochemically-treated celluloses to be significantly enhanced. The effects could not be attributed to lowering of DP; it was concluded that other chemical changes in the cellulose were probably important. In other experiments, without irradiation, it was found that even better results were obtained from samples which had been treated with 10 percent sodium hydroxide,

or from samples which had been ball-milled to a small particle size, in agreement with the work of others.

While some of the photochemical pretreatments showed beneficial effects in accelerating bacterial protein production, the quantum efficiencies did not appear to be sufficiently high to be of practical value for treatment of cellulosic wastes. However, it is possible that significant benefits could be obtained by less costly chemical treatments as well as by alkali swelling or by ball milling.

Overall, the conclusions reached from the study can be summarized as follows:

1. Cellulose, whether in the form of dry paper sheets or as aqueous slurries, can be degraded by ultraviolet radiation in the 350 to 250 nm wavelength range. The rate of the photodegradation is greatest for the shortest wavelengths and the rate is usually increased if sodium nitrite is present.

2. In the case of cellulose slurries, the rate of photodegradation can be increased by acidification of the solution with a small quantity of sulfuric acid. It is probable that a volatile intermediate is formed since the rate of photodegradation is lowered by bubbling either nitrogen or oxygen through the slurry. On the other hand, it appears that oxygen can be a reactant since the rate is lowered less by bubbling oxygen than by bubbling nitrogen.

3. The apparent quantum efficiencies for the photodegradations in terms of number of chain scissions per quantum do not appear to exceed 0.01 even in the most favorable cases.

4. From studies on the growth of microorganisms on pretreated cellulose, it appears that pretreatments involving ultraviolet irradiation in the presence

of oxygen, particularly of slurries containing sulfuric acid without sodium nitrite, or sulfuric acid with sodium nitrite and bubbling oxygen, can be beneficial in increasing the rate of protein production. However, since the benefits do not appear to be related to lowered degree of polymerization, they must be attributed to chemical changes in the cellulose. These chemical changes could probably be brought about more effectively by chemical rather than photochemical means.

5. While certain photochemical pretreatments of the cellulose increased the rate of conversion to protein, better results were obtained from two other pretreatments both of which were believed to reduce the degree of order in the cellulose fibers. These were swelling in caustic soda and ball milling.

6. The conversion of cellulose to protein by microorganisms can be enhanced by chemical changes, by swelling and by grinding. Each of these methods of modifying cellulose should be studied further if conversion of cellulose to protein is to become a means of recycling cellulosic wastes. On the other hand, photodegradation, whether nitrite accelerated or not, does not appear to be a promising pretreatment.

THE NITRITE-ACCELERATED PHOTOCHEMICAL DEGRADATION OF CELLULOSE AS A PRETREATMENT FOR MICROBIOLOGICAL CONVERSION TO PROTEIN

Abraham Fookson and Geoffrey Frohnsdorff

I. INTRODUCTION

Cellulosic materials, mostly paper and board, constitute about half of the total urban refuse in the United States[1]. The disposal of these potentially valuable cellulosic materials as trash is wasteful and contrary to national policy. For this reason, there is a need to find a practical means for converting waste cellulose into useful products.

Of the paper refuse, only the long fiber cellulose is suitable for direct recycling as paper. The remainder, the major portion of the cellulose, is not suitable for paper manufacture and it is this portion that poses the challenge for the development of new uses.

A number of concepts for the conversion of waste cellulose into useful products have been proposed. For example, Porteous[2] outlined a process in which waste paper, separated from other trash, would be hydrolyzed to glucose with dilute acid, neutralized, then fermented to alcohols, mainly ethanol. This process is not, at present, economically attractive, though it might become so if the balance between the supply and demand for ethanol should change.

Other possibilities serve to convert the cellulose into edible protein through the agency of cellulolytic microorganisms[3,4] or to hydrolyze cellulose to glucose through the agency of enzymes[5]. In the first of these, the cellulose, possibly after some pretreatment, is employed as the carbon source for the

nism's growth. Both fungi and bacteria[3,4] have been employed as the microorganisms and good quality protein has been obtained.

A study of the effects of pretreatments of cellulose on protein production by fermentation with Aspergillus fumigatus was carried out by Rogers et al[6,7]. The pretreatments used were alkali treatment, high temperature hydrolysis, electron irradiation and irradiation with ultraviolet following treatment with sodium nitrite. Only the last of them, the nitrite-accelerated photodegradation, was effective in improving the yield of protein. As a result of this finding, it was important to investigate in more detail the effect of ultraviolet irradiation on nitrite treated cellulose and the effect of the irradiation on uses for the cellulose, such as protein production. The specific objectives were to study the effects of varying the parameters incident to such irradiation, such as the nitrite concentration, the wavelength of the irradiating radiation, the duration of the irradiation and others, with a view to maximizing the amount of degradation, and then to study the utility of the degraded celluloses so obtained as substrates for the production of protein by microorganisms.

II. BACKGROUND INFORMATION

It has long been known that cellulosic materials (e.g. paper and cotton) can be degraded by ultraviolet and other radiation[8] and that the materials can also be degraded by microorganisms[9]. In general, degradation has been considered undesirable and effects have been made to combat it. However, now that there is a need to take advantage of degradative processes to aid the use of cellulosic wastes, the large amount of existing knowledge of factors affecting the degradation of cellulose can be drawn upon. In this section, attention will be drawn to important findings relevant to the studies reported here.

Cellulose is a generic name for high molecular weight poly(1,4-β-glucopyranose) in which the number of linked glucose (glucopyranose) units in the chain is usually between about 100 and 3,000. The number of linked units is termed the degree of polymerization (DP). The degradation of cellulose usually means the lowering of the DP by chain scission and it may take place either with or without substantial chemical changes to the glucose units remaining in the chain fragments[10].

The properties of a real cellulose depend upon its DP and upon the arrangement of its chains in the solid substance. They also reflect the extent to which units in the chains have been modified from the ideal as, for example, by oxidation. Natural celluloses, like most high polymers, are composed of highly ordered (crystalline) regions and poorly ordered (amorphous) regions[11]. The relative proportions of the crystalline and amorphous regions vary with the source of the cellulose and they can be changed by suitable chemical and physical treatments[12,13,14]. The degree of crystallinity affects the reactivity of the cellulose with various reagents. In general, the higher the degree of

crystallinity, the lower the reactivity. This is believed to be because the access of the reagents to the interior of the cellulose is easiest through the less ordered amorphous regions.

The packing of the molecular chains in solid cellulose has been studied by several workers. At present, there are two main schools of thought. The first postulates that the chains tend to be elongated, rather than coiled, with the roughly-parallel chains sometimes falling into virtually perfect order to form crystalline regions, while elsewhere they lose their parallelism and perfection of order to form amorphous regions[15]. The second view is that groups of parallel chains in a crystalline region form a flattened spiral super-structure of quite well-defined characteristic dimensions[16]. The exact details of the cellulose structure, other than the general distinction between crystalline and amorphous regions, are not critical to the interpretation of the work to be described in the later sections of this report.

Several treatments which are known to modify the degree of order of celluloses are solution and precipitation, swelling and deswelling, and mechanical action. As will be seen later in this section, there is evidence that these treatments can make cellulose more susceptible to microbiological attack. The best known solvents are strongly alkaline liquids such as concentrated caustic soda solution, liquid ammonia, solutions of cuprammonium or cupriethylene diamine salts, and cadoxene, or strongly acidic liquids such as concentrated sulfuric or phosphoric acids. Swelling agents may be dilute aqueous solutions of the solvents just mentioned, or many hydrogen bonding liquids or liquids with high dielectric constants, e.g., water, dimethyl formamide, dioxane, sulfur dioxide, etc.[17].

The photodegradation (phototendering) of cotton has been extensively studied. One of the most important findings which has been made is that the rate of degradation by a given radiation source can often be enhanced by the presence of a sensitizer such as an anthraquinone vat dye[18,19]. In the absence of sensitizers or other perturbing species, the quantum efficiency of the degradation (chain scission) of cellulose by light increases with the quantum energy; it is very low in the visible spectrum (700 to 400 nm) but becomes significant in the near and middle ultraviolet (400 to 200 nm). The primary photochemical reaction leading to scission appears to be the formation of a free radical with a long life which can subsequently react either with atmospheric oxygen to complete a photooxidation or with other cellulose chains to form cross-links. The fact that cellulose has no obvious absorption bands in the 700 to 250 nm region of the spectrum complicates the interpretation of the unsensitized photodegradation and it has been postulated, though not proven, that the hemiacetal grouping acts as a weak chromophore absorbing at about 250 nm and capable of forming free radicals. There is also some evidence that cellulose can even form free radicals when irradiated with visible light and this has been tentatively ascribed to absorption by conduction bands in the cellulose. However, such irradiation does not seem to cause any detectable amount of degradation.

In the sensitized photodegradation of cellulose, it appears that the usual mechanism is for the sensitizer to absorb the active radiation and form a free radical which can subsequently abstract a hydrogen atom from the cellulose[18]. In this way the cellulose acquires a free radical which can react in any one of a number of ways depending upon its environment. A likely reaction in many circumstances is reaction with oxygen to give, eventually, oxygen-containing functional groups such as carbonyl and carboxyl, sometimes with

chain scission, and possibly with propagation of the radical chain. The sensitizer is normally oxidized back from its reduced state by atmospheric oxygen and can then initiate the process once more. The best known sensitizers are certain dyes and inorganic pigments (e.g. titanium dioxide)[18].

A significant discovery about the photodegradation of cellulose (and other carbohydrates) was made by Rader and Schwartz in the early 1960's[20]. This was that the degradation by radiation of about 350 nm wavelength was much accelerated if the cellulose was first treated with a sodium nitrite solution to give about a 1% add-on of the nitrite after drying. The increase in the rate of degradation was much greater than for all of a wide range of organic compounds expected to function as sensitizers and greater than for all of a wide range of inorganic salts. Of the salts tested, only ferric chloride and certain other nitrites (e.g. potassium, calcium, ammonium) approached sodium nitrite in their effectiveness. Rader and Schwartz also found that the sodium nitrite disappeared from the system during the irradiation, presumably due to decomposition, and that carbonyl and carboxyl groups were formed on the cellulose in numbers roughly equivalent to the number of sodium nitrite molecules lost. Thus it appeared that the sodium nitrite was participating in an irreversible reaction rather than acting as a sensitizer which could be alternately reduced and oxidized in a reversible manner.

The ultraviolet absorption spectra of sodium nitrite both in the solid state and in aqueous s lution have been determined[21,22]. In both physical states, the spectrum shows a roughly uniform absorption between about 370 and 250 nm though there are weak maxima at about 360 and 310 nm and an intense absorption at about 210 nm. While the absorption of sodium nitrite in the 350 to 250 nm range is weak, it is stronger than the absorption of cellulose. It would be unlikely that it could accelerate the photodegradation of cellulose if this were not so.

The biological degradation of cellulose has been studied by many including Reese[5], Mandels[5], Callihan and Dunlap[3], and Rogers[6]. Reese, as well as Mandels, have paid particular attention to enzymatic degradation (hydrolysis), while Dunlap[3,23] has investigated bacterial attack as a method for converting cellulose to protein, and Rogers[6] has looked at fungi from the same point of view. In a review, Cowling[24] discussed the various factors which affected the rate of enzymatic attack of cellulose and drew attention to the accessibility of the cellulose to enzymes and the effects of functional groups which might be introduced into the cellulose chains. In general, any treatment which decreased the degree of order in the cellulose (e.g. treatment with swelling agents, grinding, etc.) tended to favor enzymatic attack. Similarly, functional groups which promoted swelling or decreased the degree of order favored enzymatic attack, provided they did not mask all the usual points of attack. Kaplan et al[25] showed that weathering of cellulose, which includes the photochemical effects of sunlight upon it, reduces its susceptibility to enzymatic attack. It is possible that this might be due to crosslinking or to the formation of functional groups which hinder the attack. In other work, Mandels has shown that grinding of cellulose can significantly increase the rate of subsequent enzymatic hydrolysis. Callihan and Dunlap's work[3] has been concerned with the conversion of cellulosic wastes, particularly bagasse, to single cell protein through bacterial action. They found that the rate of protein production could be improved if the bagasse, after chopping to a maximum dimension of about 1/8 inch, was treated with caustic soda solution and washed. It was suggested that the function of the alkaline treatment was to cause the cellulose to swell and open up the non-cellulosic matrix. In work with fungi, Rogers[7] found that a procedure based on the nitrite accelerated photodegradation of cellulose discovered by Rader and Schwartz was the most effective of the four

pretreatments he investigated in increasing the rate of protein production. In his work, he exposed slurries of cellulose in dilute sodium nitrite solutions to the radiation from a bank of mercury vapor lamps. The slurries, which were spread out about 1/4 inch deep in stainless steel trays and were turned over with a spatula every few hours, tended to dry out during the irradiation.

Of course, it is well known that glucose, the ultimate hydrolysis product of cellulose, is a better carbon source for bacteria and fungi than cellulose itself. Indeed, it has been shown that glucose is an intermediate product formed in the use of cellulose as a nutrient by microorganisms. It therefore seemed likely that any pretreatment which would bring about at least a partial degradation of cellulose prior to microbiological attack would favor the attack. This was a possible explanation of Roger's results. The encouraging results of Roger's work suggested the need for a more extensive investigation of the nitrite photodegradation of cellulose so as to identify the important variables in the process and to aid the technical assessment of its potential as a pretreatment prior to microbiological conversion to protein.

Other investigations of pretreatments of cellulosic materials for other purposes have been carried out by several workers. Of particular interest are those of Millett et al[26] who showed that the digestion of wood chips by cattle could be increased by treatment with caustic soda, or with liquid ammonia, or by grinding. Since digestion in the rumen of cattle involves enzymatic hydrolysis, the results of Millett may be relevant to the general problem of increasing the rate of microbiological attack of cellulose. On the other hand,

the main function of the alkaline attack, or the grinding, may have been to open up the lignin matrix which effectively encapsulates the cellulose fibers in wood.

In the light of the information reviewed here, it is apparent that pretreatments which may promote the microbiological attack of cellulose are:

1. Nitrite photodegradation
2. Alkali treatment
3. Grinding

In the work described in the following pages, the emphasis is on the first of these but, for comparison, the other two have been included in a small number of experiments.

III. EXPERIMENTAL

The purpose of the experimental work was to find out how rapidly cellulose in the form of paper sheets or aqueous slurries could be degraded by ultraviolet irradiation in the presence of sodium nitrite and to investigate the effects of photochemical pretreatment on the subsequent conversion of the cellulose to protein by microorganisms. The cellulose substrates were high purity commercial products consisting of a cotton linters filter paper and two purified wood celluloses (see Appendix). The main variables to be investigated were the wave length and time of the radiation, the concentration of sodium nitrite and, for the slurries, the pH and the presence or absence of oxygen. For comparison purposes, two non-photochemical treatments consisting of alkali swelling in one case and ball-milling in the other were also applied to the wood cellulose. The equipment and the experimental details are described in the Appendix.

The studies of the effects of the pretreatments on the conversion of wood cellulose to protein were carried out in other laboratories. The fungal growth tests were carried out at the Cincinatti Laboratories of the Environmental Protection Agency under the direction of Mr. Charles Rogers while the bacterial growth tests were carried out at the Louisiana State University under the direction of Dr. Charles Dunlap.

IV. RESULTS AND DISCUSSION

A. Actinometry of the reactor

In order to be able to intercompare the results of the irradiation of samples at different locations in the reactor, and also to make possible estimates of the energy needed to degrade the cellulose to various degrees in different treatments, actinometric measurements were carried out.

The intensity of radiant energy was measured as described for the three sets of lamps (nominal wavelengths of 254 nm, 300 nm, and 350 nm). The results are shown in Table 1. It can be seen that in the center position, the 125 ml of actinometer solutions received from 6×10^{15} to 8×10^{15} quanta ml^{-1} sec^{-1}, while the merry-go-round position received between 2×10^{16} and 3×10^{16} quanta ml^{-1} sec^{-1}. Thus, no major differences in photochemical effects on substrates being irradiated would be expected which could be attributed to differences in radiation intensity among the three sets of lamps.

These values were used to calculate apparent quantum efficiencies among irradiation runs. The actinometer solutions are transparent and, under the conditions employed here, substantially 100 percent of the incident radiation is absorbed by the solution.[2] This is certainly not the case with the cellulose slurries for which some of the incident radiation is undoubtedly lost through reflection and scattering. Thus, for the conditions encountered in this work, the values in Table 1 represent the maximum radiation falling upon the cellulose substrates, rather than the actual radiation which was effective in the radiative degradations.

B. Irradiation of dry cotton linters paper

The first cellulosic material to be studied was the cotton linters paper. This could be handled in essentially the same way as the dry cotton fabric

samples previously studied by Rader and Schwartz[20] so it made a good starting point for an extension of their work. The objective was to determine what factors affected the rate of degration and how far the DP of the cellulose could be lowered.

The effect of irradiation of various wavelengths upon untreated cotton linters paper is shown in Figure 1. It can be seen that the more energetic the radiation, i.e., the shorter the wavelength, the more the DP was reduced in any given time. Also, the rate of degradation gradually decreased with increasing irradiation time, as shown by the levelling out of the curves; this effect was more pronounced at 300 nm and 350 nm than at 254 nm.

With 1 percent add-on of sodium nitrite, however, the effects of irradiation differed from that shown in Figure 1 in two important respects, as seen in Figure 2. One is that the differences due to different wavelengths practically disappeared, the three curves in Figure 2 being almost concurrent. The second is that the rates of degradation during the earlier periods of the irradiations, i.e., during the first hour, were extremely rapid, and levelled off sharply thereafter. The rapid reduction in DP in Figure 2 is in marked contrast to the more gradual reductions shown in Figure 1.

Figure 3 shows the results obtained in a more detailed study of the effects of irradiation of nitrite-sensitized cotton linters paper at 254 nm. In this group of experiments, the amount of sodium nitrite add-on and the intensity of the radiation were varied. The sodium nitrite add-ons ranged from 0 percent to 10 percent of the weight of the paper. Two radiation intensities were studied, one obtained by using all 16 lamps and the other by removing every other lamp, to leave eight. Samples were removed at intervals from the reactor, up to 24 hours, and the amount of degradation assessed by measuring the DP.

It can be seen that all of the samples, including the one with no sodium nitrite, had been degraded. However, as discussed above in connection with Figures 1 and 2, the effect of the nitrite acceleration is clearly evident. Whereas the curve for the untreated paper shows a gradual decline in DP, with no rapid changes in slope, those of the treated papers indicate an initial rapid decrease in DP and a subsequent levelling off. Further, these effects became more pronounced the higher the concentration of sodium nitrite.

It is evident from Figure 3 that, whereas the decrease in DP from no nitrite or 0.1 percent nitrite to 1 percent nitrite is appreciable, the increase from 1 percent to 10 percent nitrite produced a much smaller effect. This is seen more easily in Figure 4, where the data are presented in terms of the average number of chain scissions per molecule as calculated by the method of Sakurada and Okamura.[27] This emphasizes the differences in rates of chain scission with time and with nitrite content.

The effects on the DP of altering the light intensity by removing half of the lamps are also shown in Figure 3. It can be seen that, in the case of the 0.1 percent sodium nitrite-treated papers, the effect of the higher intensity was to produce more degradation than did the lower intensity for equal irradiation times. With 1 percent sodium nitrite add-on, however, no perceptible difference in the effects on degradation of the two levels of irradiation could be perceived, within times ranging up to 24 hours. Thus, both sets of irradiation conditions at 1 percent add-on are shown as one curve in Figure 3 (second curve from the bottom in the figure).

Though the matter was not investigated in detail, evidence that the degradation of the paper was associated with the depletion of the sodium nitrite is shown in Figure 5. This curve shows the amount of residual sodium nitrite in papers originally containing 1 percent sodium nitrite, following various

irradiation times up to 24 hours, at the three available wavelengths. The apparent similarity between the curve shapes of Figure 2, which shows the decrease in DP with irradiation, and Figure 5, which shows the disappearance of nitrite, suggests that the phenomena are closely related. These results obtained with cotton linters paper are consistent with the data of Schwartz and Rader (20) obtained with cotton fabric, showing a quantitative relationship between nitrite loss from irradiated treated cotton and the number of chain scissions per cellulose molecule.

The rapid disappearance of the nitrite ion shown in Figure 5 may be due to rapid oxidation of the nitrite to nitrate but, alternatively, it might be associated with the oxidation of the cellulose by photochemically excited nitrite which becomes reduced in the process.

Overall, the studies of the degradation of the dry cotton linters paper with and without sodium nitrite showed that, at least initially, the nitrite acted as an effective accelerator of the photochemical degradation. On the other hand, the effect of the nitrite was rapidly dminished during irradiation. This may have been due to decomposition of the nitrite or to non-uniform distribution of the nitrite in the cellulose structure, or both.

Another salt which had been reported[20] to be effective in promoting the photodegradation of cotton cellulose was ferric chloride. To check whether this was so for paper, experiments similar to these described using sodium nitrite were carried out. The ferric chloride levels used were 0.05 percent, 0.2 percent, and 1 percent add-on. No sensitizing action was observed, as can be seen from Figures 6 and 7. Indeed, comparison of Figure 7 with Figure 1 suggests that ferric chloride may have a slight inhibiting effect on the degradation. For this reason, ferric chloride was excluded from the later studies.

C. Cellulose suspensions

1. Cotton linters paper.

The study of the photochemical degradation of air-dry paper which had been treated with sodium nitrite confirmed earlier work[20] as to the potency of this material as a sensitizer for the photochemical degradation of cellulose. However, if thought was to be given to the employment of irradiation as a step in the conversion of waste cellulose into other useful products, better means of exposure to the source than as a dry sheet was desirable. One of the problems, for example, is the fact that the paper scatters so much radiation that the degradation occurs only in a thin layer at the surface.[28] Thus, for efficient conversion, the paper would have to be presented to the irradiating source in thin sheets; in view of the enormous volume of waste paper for which such processes should be useful, this would be extremely difficult.

Irradiation of the cellulose in the form of an aqueous slurry or suspension of comminuted particles, which could be stirred during the exposure, appears as an attractive way of insuring that all of the substrate would be irradiated equally. In such a system, the sodium nitrite could be incorporated into the aqueous dispersion medium, as could any other additives found desirable. Thus, all of the work described in the following relates to the irradiation of slurries and the results obtained therefrom.

It was of importance to learn whether or not short-time nitrite-sensitized irradiations of slurries, such as one hour, would result in marked reductions in DP, as occurred in the case of the cotton linters paper. To this end, a slurry prepared from this paper in sodium nitrite solution was irradiated.

By stirring cotton linters paper with water or sodium nitrite solution in an Osterizer (essentially a device similar to the more familiar Waring Blendor), the paper was readily pulped down to its constituent fibers (determined by microscopic examination before and after pulping). This

yielded a slurry which was quite thick at 3 percent paper content. The 1 percent slurry was found to be more tractable for stirring with a laboratory magnetic stirrer.

A slurry consisting of 1.01 g of paper in 120 ml of 0.84 percent sodium nitrite, or 0.83 percent paper content, was irradiated in the Rayonet reactor for one hour at 254 nm. After filtering washing, and drying, the filtrate had a DP of 1070, as compared to 1170 before the irradiation. The pH of the filtrate was 6.5, whereas that of the slurry before irradiation was 6.4 Thus, one hour's irradiation under the conditions described produced negligible change in the material, unlike that found with the dry paper (see, for example, Figure 2).

2. Wood pulp cellulose

No further work was done with paper pulp slurries. Instead, slurries were made with two grades of Solka-floc, a commercially available, purified wood pulp cellulose. The grades are designated SW-40 and SW-200 (see Appendix). Since both are obtained as powders, comminution was unnecessary unless further reduction in particle size was desired. SW-40 and SW-200 are manufactured to well-defined specifications and they differ primarily in particle size, SW-200 being the finer. As a result, the two materials were quite different in their properties and behavior. Thus, the physical appearances of the dry powders were different, the BW-200 being more free-flowing, and they behaved quite differently in slurries. For example, at 3 percent solids content, SW-40 slurries were difficult to stir, while those with BW-200 were still quite fluid even at 10 percent solids. In addition, as will be shown below, they exhibited somewhat different behavior toward the degradative conditions to which they were subjected. The appearance of the particles under magnification are shown in Figure 8 (SW-40) and Figure 9 (BW-200). The presence of many long particles in the SW-40 can be clearly seen.

a. Effect of nitrite concentration. The variables which were studied in the degradation of the slurries were the wavelength, irradiation time, nitrite concentration, slurry concentration, pH, and presence or absence of oxygen. In most cases, the properties which were monitored were the DP, the pH of the aqueous medium and the weight loss of the solid. The effects of the variables will be discussed in turn.

Table 2 shows the DP of the washed and air-dried filter cakes following the irradiation of SW-40 slurries in sodium nitrite solutions of 0, 1, and 10 percent (w/v) concentrations. The slurries contained 2.7 percent and 1.5 percent cellulose (w/v). It can be seen that the lowest DP values were obtained at the 1 percent sodium nitrite concentration, for both slurry concentrations, the effect becoming more pronounced the longer the duration of the irradiation. In fact, the degradation in 10 percent sodium nitrite was, at best, no greater than that found with no sodium nitrite. Reasons for the existence of a maximum in the cellulose degradation in solutions of about 1 percent sodium nitrite concentration will be considered below, when the fate of the sodium nitrite as a result of the irradiation is discussed.

The effect of sodium nitrite concentrations of less than 1 percent is shown in Table 3, for 2.7 percent SW-40 or BW-200 Solka-floc in sodium nitrite solutions irradiated for 19 hr at 254 nm. and in Table 4, for 10 percent BW-200 Solka-floc irradiated for 19 hours and 48 hours at 254 nm. In Table 4, the number of scissions per molecule corresponding to each DP is also listed for illustration. Within this concentration range, the data show that the DP decreased as the concentration of sodium nitrite increased, the effect being more pronounced with the SW-40 cellulose than with the BW-200. Thus, with the former, the DP after irradiation fell from 400 to 290 as the sodium nitrite concentration changed from zero to 1 percent.

In Table 4, the same small effect of increasing degradation as the nitrite concentration increased from 0 to 1 percent can be seen for the 19-hr irradiation of the 10 percent slurry, similar to that of the 2.7 percent BW-200 slurry in Table 3. The effect in Table 4, however, is unambiguous at the 48-hr irradiation time.

Considering the data in Tables 2 and 3, it appears that there is an optimum concentration of sodium nitrite in the slurry, at which the amount of degradation is maximized. Under the experimental conditions employed here, this optimum is of the order of 1 percent.

b. Effect of slurry concentration. In Table 5, the data for the two different slurry concentrations of the BW-200 Solka-floc, at 19-hour irradiation, are tabulated together for easier comparison. The lower DP, or greater degree of degradation, is seen as occurring at the lower slurry concentration, at each level of sodium nitrite concentration, as expected.

A similar effect was exhibited by the SW-40 Solka-floc, which can be seen when comparison is made between the results of irradiating 1.5 percent and 2.7 percent slurries. Figure 10 shows such a comparison, based upon the data in Table 2. The number of scissions per molecule were calculated, corresponding to each DP value, and plotted against irradiation time in Figure 10. Each curve represents a constant sodium nitrite concentration in the slurry, while the solid lines represent a slurry concentration of 1.5 percent Solka-floc, and the dashed lines represent 2.7 percent Solka-floc slurries. It is clear from these curves that, for any level of sodium nitrite, the 1.5 percent slurries exhibited greater degradation than did the corresponding 2.7 percent slurries. Further, the conclusion drawn earlier concerning the greatest degradation occurring in those slurries made with 1 percent sodium nitrite solutions is also illustrated. In fact, the curves for the 0 percent and the 10 percent

sodium nitrite slurries are either very close together or are superimposed, and lie below those for the 1 percent sodium nitrite slurries. Also, at the 1 percent nitrite level, the number of scissions per molecule increased linearly with time, a phenomenon not observed with the dry cotton linters paper.

c. Effect of wavelength. In Table 6 are shown the DP values obtained on 2.7 percent slurries of SW-40 Solka-floc in several different concentrations of sodium nitrite, following 19 hr irradiation at 254, 300, and 350 nm. At all levels of sodium nitrite, the most degradation occurred at 254 nm, and the least at 350 nm. At the latter wavelength the accelerating action of the sodium nitrite can be clearly seen, the DP falling from 730 at zero percent sodium nitrite to 540 in the 1 percent sodium nitrite, a drop of 26 percent. Similarly, at 254 nm, the DP fell from 400 in the absence of sodium nitrite to 290 in 1 percent sodium nitrite, a drop of 27.5 percent. No such effect was observed at 300 nm.

d. Effect of irradiation upon the pH of the filtrate and weight loss of the solid. Some indications of the nature of the transformations occurring during the irradiations may be inferred by considering the pH of the filtrates obtained from the slurries following irradiation, and the loss in weight of the cellulose. Table 7 shows the pH of the filtrates obtained from 1.5 percent slurries of SW-40 Solka-floc in sodium nitrite solutions after irradiation for various times at 254 nm.

This table shows that, at all levels of sodium nitrite concentration, the filtrates became more acidic as the duration of the irradiation increased. This tendency manifested itself after an initial rise in pH during the first 2 hours. The increase in acidity with time was most pronounced in the absence of sodium nitrite, and least pronounced in 10 percent sodium nitrite. This difference dependent upon sodium nitrite concentration is probably a consequence

of a buffering action due to the sodium nitrite. This buffering action is demonstrated in Table 8, where the pH of several reaction mixtures (which will be discussed in greater detail below) to which sulfuric acid were added are shown. It can be seen that, in the absence of sodium nitrite, the pH fell from 5.3 to 2.5, then to 2.2, upon the addition of 1 ml and 2 ml 1N sulfuric acid, respectively. When the slurries were prepared in 1 percent sodium nitrite, the initial pH was 5.6, and dropped to only 4.7 and 4.0 upon the addition of 1 ml and 2 ml acid. It can be expected that in 10 percent sodium nitrite the buffering action would be even more pronounced, as implied in Table 7.

The other phenomenon revealed in Table 7, namely, the initial rise in pH for short irradiation times, is also worthy of note. Several additional examples are given in Table 9. The behavior of the pH here parallels that found in the first two columns of pH data in Table 7. The interesting feature in Table 9 is the behavior of the 10 percent slurry with no sodium nitrite. This slurry underwent a pH change from 5.3 to 6.3 by merely stirring at room temperature for 4 hours. It is possible that the early changes in the slurries without sodium nitrite, thus devoid of buffering, shown in Tables 7 and 9, may be due to gaseous airborne laboratory contaminants. This, however, could hardly serve as an explanation for the pH changes in those slurries with sodium nitrite.

Returning to Table 7, the decrease in pH of the filtrates with increasing irradiation time is probably due to the formation of water-soluble acids as a result of photochemical oxidative degradation. This is consistent, at least qualitatively, with the findings of Beelik and Hamilton[28] in their study of the water-soluble fraction resulting from the ultraviolet irradiation of wood-cellulose sheets. They found that 25 percent of the water-soluble fraction consisted of acids; none of this material was uronic acids or other sugar acids.

The weight losses, in terms of the differences in weights between the initial charge of cellulose in the slurries and the final air-dried filter cakes, though somewhat erratic, showed a tendency to increase with increasing irradiation time, hence indicating an increasing amount of degradation. The weight losses were generally under 5 percent of the original material, but occasional values of 6 to 8 percent were encountered. The losses were assumed to be due to formation of water-soluble material, probably oligomeric moieties resulting from scissions of cellulose chains near their ends.

e. Effects of additives upon degradation. Several materials in addition to sodium nitrite were tried as additives to the cellulose-aqueous sodium nitrite slurries discussed above. They were examined because they were thought likely to affect the reactions of sodium nitrite in solution and possibly influence the course and the extent of the photochemical reactions. In particular, in addition to studying their chemical effects, it was important to determine if these changes would cause the partially degraded cellulose to be more readily utilized by microorganisms for their protein synthesis. This point will be discussed in greater detail in Section i.

In this section the effect of the presence of the other materials upon the ensuing photochemical degradation of cellulose will be considered. As in the above sections, the criterion of degradation was the lowering of DP. Table 10 shows the effect of the addition of acid or alkali upon this property. In the low concentration shown here, sodium hydroxide was investigated only in the experiment shown in the table. The drop in pH, from 11.4 before irradiation to 7.0 after 19 hours irradiation at 254 nm in 1 percent sodium nitrite was in accord with the behavior of the cellulose slurries discussed in Section d. The DP, however, exhibited no reduction below that found with no

sodium hydroxide added (top line of the table); the value found was 330, while that for the irradiated slurry with no added alkali was 300.

In the presence of sulfuric acid, however, the effect was appreciable, more so in the slurries with 1 percent sodium nitrite than without. Thus, in the presence of the sodium nitrite, the DP fell from 300 without added acid, to 160 with 0.1 percent sulfuric acid added, while in the absence of sodium nitrite the DP values were 420 and 330, without and with 0.1 percent sulfuric acid, respectively. Increasing the amount of sulfuric acid in the 1 percent sodium nitrite reaction mixture to 0.15 percent only caused the DP to be lowered from 160 (at 0.1 percent) to 150, so it appears that a plateau in the effective amount of sulfuric acid was being approached.

In several other experiments, the dissolved gases and the gaseous environment were controlled by bubbling pure oxygen or nitrogen through the reaction mixtures during the irradiations. The slurries were all 10 percent BW-200 Solka-floc in 1 percent sodium nitrite; some had no added acid, while others had 2 ml of 1N sulfuric acid added. They were all irradiated for 19 hours at 254 nm. The results, in terms of DP of the cellulose and the pH of the filtrates obtained, are shown in Table 11. The data in Table 10 for the reactions in 1 percent sodium nitrite with 0 and 0.1 percent sulfuric acid represent the control experiments for those in Table 11. The results in Table 10 are from reaction conditions like those in Table 11, except that the former experiments were carried out in ambient air rather than oxygen or nitrogen. With no added acid, the results in the ambient air atmosphere and the bubbling oxygen atmosphere were substantially the same. Thus, the two pH values were almost equal, 5.5 compared to 5.1, respectively, as were the DP values, 300 compared to 280. With 0.1 percent sulfuric acid, however, the

filtrate from the ambient air reaction had a pH of 4.5, while that from the reaction in the oxygen atmosphere was 2.3. On the other hand, the DP from the reaction in the air atmosphere was 160, while that from the oxygen atmosphere was 220, a small, but possibly significant, difference.

In the case of the reactions in the nitrogen atmospheres shown in Table 11, the DP values were somewhat lower than those reactions of similar acidity, but zero percent sodium nitrite, listed in Table 10. That is, in the nitrogen atmospheres the sodium nitrite apparently was not as effective as a photochemical accelerator, so that the degradation of the cellulose was not as extensive as under the other atmospheres discussed. No work was done to elucidate the reasons, but it may be significant that the pH values of the resulting filtrates were quite high, in both the acidified and unacidified reaction mixtures; thus, the pH of the filtrate from the reaction with no acid added was 9.5, while that from the reaction mixture which originally contained 2 ml of sulfuric acid was 8.8. These were the highest pH values found in this work for reaction mixture filtrates.

The low pH of the filtrate from the acid reaction mixture in the oxygen atmosphere would indicate more extensive oxidation of the cellulose to carboxyl than occurred either in the air environment or the non-acidified reaction mixtures. In particular, some oxidation would have to occur at or near the chain ends, thus giving rise to low molecular weight, water-soluble acids, which appear in the filtrate.

f. Behavior of the sodium nitrite in the reactions. From the point of view of the understanding of the reactions, and for evaluating the economics of the nitrite-sensitized photodegradation of cellulose,

the behavior of the sodium nitrite, including its durability, is of interest. Several aspects of this problem were studied.

Table 12 shows the results obtained when a 0.25 percent solution of sodium nitrite was irradiated with 254 mm radiation in the reactor for a period of about 22 hours, samples being drawn periodically during the irradiation and analyzed for nitrite and the pH measured. This particular concentration of sodium nitrite was chosen for convenience in dilution when preparing the samples for analysis by the method of Hartley and Asai[29]. It can be seen that, within several hundredths of a percentage point, the concentration did not change over the 22-hour irradiation period. Similarly, the pH remained constant over this period. Thus, it can be concluded that the sodium nitrite, by itself, is stable to radiation under the conditions employed for irradiating the cellulose in this work.

The nitrite was not so stable when other materials were present. In the presence of cellulose, sometimes with the gaseous or sulfuric acid additives described in Tables 10 and 11, some of the nitrite originally present in the reaction mixtures was destroyed following 19 hours' irradiation at 254 mm. This was revealed upon analyzing the filtrates as shown in Table 13.

In all of the reaction mixtures in Table 13, the cellulose (10g of BW-200 Solka-floc) was dispersed in 100 ml of 1 percent sodium nitrite. Thus, the concentration of sodium nitrite in grams per 100 ml of solution, or percent, as listed in the table, was numerically equal to the weight in grams of the sodium nitrite present. By subtracting these values from unity the amount of sodium nitrite consumed can be calculated. From this, together with the average number of scissions per molecule and the molecular weight of Solka-floc, the number of molecules of sodium nitrite consumed per scission was calculated; this is shown as the last column in the table.

It can be seen that in acid medium and in the presence of oxygen (still air or oxygen atmosphere) most of the nitrite was consumed during the course of the reaction. In the absence of oxygen, such as the acid medium with the nitrogen atmosphere, as much as 35 percent was consumed, and in the nitrogen atmosphere without acid 13 percent of the nitrite vanished. For any atmosphere, there was greater destruction of nitrite in acid medium than without acid.

There was no simple correlation between the concentration of sodium nitrite remaining and the pH of the respective filtrates. Thus, two filtrates of pH 4.5 and 2.3 had concentrations of 0.13 percent and 0.12 percent sodium nitrite, respectively. Similarly, filtrates with pH values of 8.8, 5.5, and 5.1 were 0.65 percent, 0.68 percent and 0.64 percent in sodium nitrite respectively.

The number of molecules of sodium nitrite consumed per scission ranged from 8.6 to 27.0, for which no simple stoichiometry is evident. Roughly, the greater the average number of scissions per molecule, the more nitrite was consumed per scission. The lowest DP values, and thus the highest nitrite consumption, were associated with the acidic media and oxygen-containing environments.

Another question raised by the presence of sodium nitrite in the slurries being irradiated is the extent to which the cellulose substrate is shielded from the radiation due to absorption by the solution at the wavelengths of interest. The absorbances of a number of filtrates were measured in the Beckman DU spectrophotometer at 254 nm, 300 nm, and 350 nm using 10 mm cuvettes. The filtrates were from irradiated slurries of SW-40 Solka-floc, initially containing zero, 1, and 10 percent sodium nitrite, and irradiated at either 254 nm or 300 nm. As controls, unirradiated 1 percent and 10 percent solutions of sodium nitrite, containing no cellulose, were also measured. The results are shown in Table 14.

All of the filtrates were clear in this work, but those from irradiation reactions in the absence of sodium nitrite were, in addition, water-white. Those with 1 percent sodium nitrite had a pale yellow cast, while those with 10 percent sodium nitrite were deeper yellow, possibly due to small quantities of nitrogen oxides or colored organic moieties from the cellulose interacting with the sodium nitrite. Since these may be expected to absorb in the ultraviolet, the absorbance values of the filtrates in Table 14 should not be construed as a precise analytical measure of the amount of sodium nitrite present.

Solutions 1 and 2 in the table, which were 1 percent and 10 percent sodium nitrite solutions, exhibited high absorbances at all three wavelengths, the 10 percent solution being beyond the range of the spectrophotometer. Further, solutions 9 and 10 which were filtrates from irradiation reactions in the absence of sodium nitrite, showed very low absorbances, indicating that the water-soluble reaction products contributed little to the absorption of the radiation. On the other hand, solutions 3 and 5, which were filtrates from slurries with 1 percent sodium nitrite irradiated at 254 nm and 300 nm, respectively, exhibited absorbances very much like solution 1, the 1 percent sodium nitrite solution, with possibly a small but unknown contribution due to water-soluble reaction products. In like manner, solutions 4 and 6 can be compared with solution 2, the 10 percent sodium nitrite solution.

Solutions 4 and 6 were diluted by a factor of 10 with water, to give solutions 7 and 8, respectively; these latter two should be equivalent to 1 percent sodium nitrite solutions. Their absorbances are indeed very much like the filtrate from the 1 percent sodium nitrite slurries, solutions 3 and 5. This indicates that Beer's Law is valid for these solutions, and that the values "greater than 3.00" listed for the absorbances of the 10 percent filtrates actually represent almost total opacity for a 10 mm path length

at the given wavelengths. This attenuation of the radiation may explain why those slurries with 10 percent sodium nitrite underwent less degradation than those with lower nitrite concentrations, as shown in Table 2. Due to the high absorption, the photochemical reaction can occur only in a thin annular volume at the walls of the quartz reaction vessel. Hence the result appears to represent the opposing effects of the absorption of the radiation by the nitrite and the diminution of the quantity of cellulose in the volume in which absorption takes place.

g. Quantum efficiencies. Employing the actinometric data of Table 1, the geometry of the reactor, sample size, and irradiation time, it is possible to estimate the apparent efficiency of the photochemical degradation in terms of the apparent number of quanta required per scission. The estimates are necessarily rough because of the considerations of the opacity of the cellulose slurries or paper strips, and light scattering, discussed above in Section IVA. Corrections were not made for these factors nor for the absorption by the sodium nitrite. Thus the quantity calculated here is the amount of energy incident on the system, per scission.

Table 15 gives the quantum efficiencies, as so defined, for the irradiation at 254 nm of a series of cotton linters paper strips with 1 percent sodium nitrite add-on. It can be seen that the number of quanta per scission was quite high. Further, the number of quanta per scission increased as the irradiation proceeded. This behavior can also be inferred from Figure 6, where, after the initial rapid drop in DP, the rate of depolymerization fell sharply. This implied that since the irradiation proceeded at the same rate, in terms of energy per unit time, the number of scissions per unit time decreased.

In the irradiation of slurries the initial quantum efficiencies encountered were, in general, between the smallest and largest found in the irradiation of papers. This is so because, in the case of the slurries, the depolymerization rate did not change as markedly with time of irradiation as it did in the case of the papers.

Table 16 shows the quantum efficiencies found in the irradiation at 254 nm, of 1.5 percent and 2.7 percent SW-40 Solka-floc slurries in 1 percent sodium nitrite solution, for various times. It can be seen that the efficiencies of the reaction at the two concentrations are almost the same, with a slightly higher efficiency for the more concentrated slurry.

In irradiating the finer particle size Solka-floc, the BW-200, the efficiencies during the earlier periods of the reaction were higher than with the SW-40. As the irradiations progressed and the number of scissions per unit time decreased, the two tended to equalize. This can be seen in Table 17, by comparing it with the data on the 2.7 percent slurries in Table 16. Greater quantum efficiencies were obtained with 10 percent slurries of BW-200 Solka-floc, as shown in Table 18. In this table the superior influence of 1 percent sodium nitrite over that of lower concentrations can be clearly seen. Further, through the use of additives, such as 1N sulfuric acid, in addition to the sodium nitrite, lower DP's are obtained in a 19-hr irradiation time (Table 10). This results in even greater quantum efficiencies, as the data in Table 18 shows.

By comparing Tables 16, 17, and 18 with Table 15, the conclusion can be drawn that quantum efficiencies which are at least as high as those obtained by irradiating dry papers can be obtained in the irradiation of slurries, particularly if larger numbers of scissions per molecule are sought. This is an important finding, since the handling of slurries offers many advantages over the manipulation of dry papers.

h. Measurements of accessibility. Since the accessibility of the cellulose is known to affect the rate of many reactions, it was of interest to know if there were significant differences in the accessibilities of the materials used in the present study. The results obtained for the cotton linters paper and the two purified wood celluloses using the deuterium exchange method are given in Table 19. It can be seen that all three materials have a high accessibility to deuterium oxide, with the wood celluloses giving higher values (88% for SW-40 and 82% for BW-200) than the cotton linters paper (66%). The higher values for the wood celluloses may reflect the effects of the grinding which the wood celluloses are known to be subjected to in preparation, though it could also reflect the different plant origin.

The relatively small difference in the accessibilities of the two wood celluloses suggests that it is unlikely to cause any large differences in behavior. This appears to be consistent with the fact that, in the 254 nm photodegradation of slurries in 1% sodium nitrite solutions, the two materials behave similarly with only a slightly higher rate and apparent quantum efficiency being observed for the BW-200 (see Tables 3, 16 and 17). Clearly, the difference in particle sizes (see Figures 14 and 15) does not appear to be an important factor though it may account for the slightly smaller degree of degradation of the coarser SW-40.

The 66% accessibility of the cotton linters may be compared with values obtained for cotton linters by other workers[30,31]. Using a deuterium exchange method similar to that used in the present work, Frilette, Hanle, and Mark[30] obtained a value of 61%. This is consistent with the present value. On the other hand, Frilette and his coworkers obtained an accessibility value of only 5% when using the acid hydrolysis method. This low value was close to the 5.8% obtained by Nelson and Conrad[31], using the same method. These

results illustrate the difficulty in making definitive accessibility measurements, because the accessibility varies with the dimensions of the species used and the conditions chosen for the measurements. The higher values obtained using deuterium exchange are probably a result of the ability of deuterium oxide to penetrate the crystalline regions to a significant extent and to produce some exchange there as well as the essentially complete exchange in the amorphous regions. In this connection, it may be noted that Mann and Marrinan[32] found that about 33% of the hydroxyl groups in the crystalline regions of viscose may be deuterated within four hours. Although it is likely that a similar penetration occurred in the samples of the present study, this does not affect the usefulness of the tabulated results as comparative values showing the relative accessibilities to small molecular species such as water and, probably, sodium nitrite.

i. Use of photodegraded celluloses as substrates for fungal and bacterial growth. The main part of the program described in this report was the study of the parameters affecting the nitrite-accelerated photodegradation of cellulosic substrates. However, in accord with the objective of the conversion of waste cellulose, particularly paper, into useful products, many of the degraded celluloses from the ultraviolet irradiations were tested as substrates for the growth of selected fungi or bacteria, as a means for generating edible protein.

The tests with the fungi were carried out at the laboratories of the National Environmental Research Center, Cincinnati, Ohio, under the direction of Mr. Charles Rogers. The organism employed was Aspergillus fumigatus. It was inoculated into a broth which, in addition to the cellulose, provided the necessary nitrogen, phosphorus, and other nutrient elements. The samples were then incubated, with mechanical shaking, for periods of up to 96 hours, following which the fungal mass was analyzed for protein.

The cellulose samples subjected to the fungal growth testing were all obtained by irradiating Solka-floc slurries. They were selected because of their differences in DP, in particle size, in the additives present during the irradiations, in whether or not the respective slurries were filtered and dried prior to shipment for fungal growth testing, and in the concentrations of cellulose and sodium nitrite in the irradiated slurries. Untreated Solka-floc was used as a control.

The percent protein obtained at the 24-hour period was in all cases about 12±3 percent of the fungal mass and showed no clear dependence on any of the variations mentioned. The variations about 12 percent could not be attributed to the systematic differences between the samples. A possible reason for the similar yields is suggested by the observation that the cellulose always appeared to be entirely utilized except, possibly, for occasional encapsulated pockets. Thus, even if there were different rates of utilization, these would not be noticed once the reactions were complete. Experiments of shorter duration would be needed to show up differences in rate.

Greater responses to variations in the treatments of the cellulose were found in the results from samples which were employed as substrates for growing a mixture of Alcaligenes faecalis and Cellulomonas, sp., bacteria. These experiments were carried out in the Department of Chemical Engineering, Louisiana State University under the direction of Dr. C. E. Dunlap. The samples included both irradiated and unirradiated slurries, dried filter cakes from slurries, and controls. The culture medium consisted of a standard aqueous solution of nitrogen- and phosphorus-containing inorganic salts, together with the cellulose sample (4g per liter in the culture medium) under test. It was inoculated with a mixed culture of Alcaligenes faecalis and Cellulomonas, sp., bacteria. The Cellulomonas was isolated from a sample of

rotting sugarcane and soil mixture according to the method of Han and Srinivasan[33], as described in the report of Callihan and Dunlap[3]. The results, after incubating at 34°C for up to 48 hours, were reported as turbidity measured in a Klett colorimeter. On this scale, the higher the turbidity, the higher the yield of cells.

The samples were subjected to bacterial culture in three groups. The results for each group are shown in separate tables: Tables 20, 21 and 22. With each group a sample of Whatman No. 1 filter paper was run as a control. Because of batch-to-batch variations, related possibly to variations in the strengths of the inocula, the Klett turbidities for the filter paper controls varied significantly. Hence it was felt that unwarranted conclusions may be drawn if attempts were made to compare Klett turbidities from one table to another. Therefore, in the following discussion, the results in each table will be considered independent of each other and will be discussed separately.

The samples in Tables 20 and 21 were all submitted for bacterial growth testing as dry powders, while those in Table 22 were submitted as slurries. The powders were the washed, dried filter cakes from the reactions whose conditions are listed in preceding tables. The slurries from which the samples of Table 22 were prepared were from reactions similar to those of Tables 20 and 21 except that, in the case of Table 22, the filter cakes, following washing after the reactions, were redispersed in water without first drying. The samples therefore contained none of the additives which may have been present during the irradiations or other treatments. As can be seen from the tables, the treatments were quite varied; some samples contained sodium nitrite and/or other additives, some were irradiated, and others were stirred without irradiation.

To judge the effectiveness of the treatments in improving the yields of bacteria, untreated samples of SW-40 and BW-200 Solka-floc as received from the manufacturer were sent for evaluation; the latter was also sent as a 10 percent slurry without irradiation. In addition, a quantity of BW-200 Solka-floc was ball-milled for 48 hours to give a material of smaller particle size, and probably lower crystallinity, than the BW-200. This was sent as a dry powder without further treatment (sample 10, Table 21), as a slurry without irradiation (sample 2, Table 22), and as a slurry following 19 hours irradiation in sodium nitrite solution (sample 1, Table 22). For those samples for which the information was available, the DP's are listed in the tables.

Table 20 shows data obtained from runs covering pH modifications and/or gaseous environment modifications. Best results were obtained with samples 1 and 6, both of which contained sulfuric acid. Increasing the amount of sulfuric acid, either with (samples 2 and 4) or without sodium nitrite (samples 1 and 3) in the reaction mixture, resulted in a lowering of the bacterial yield. Also, comparing samples 2 and 3, both of which contained 0.1 percent sulfuric acid, appears to indicate that the presence of sodium nitrite (sample 2) was detrimental to the bacterial yield unless oxygen was bubbled through (sample 6).

Stirring the Solka-floc, without irradiation, for 4, 6, or 19 hours, with or without sodium nitrite (samples 9, 10, and 11), was without effect upon the yield. The yields here were lower than those discussed above with slight acidification in the absence of sodium nitrite. These yields (Klett turbidities of 400 to 440) were the same as those obtained in an atmosphere of nitrogen with (sample 8) or without (sample 7) acidification. An oxygen atmosphere with an acidified medium (sample 6) resulted in a somewhat improved bacterial yield, Klett turbidity 550. It can also be seen from Table 20 that

there are no effects on the bacterial yield which can be attributed to differences in DP.

Table 21 shows that good yields of bacteria were obtained from Solka-floc samples which had been irradiated without additives other than sodium nitrite (samples 2, 3, 4, and 5); 19 hours irradiation was somewhat superior to 48 hours, and the presence or absence of sodium nitrite appeared to be immaterial. However, equally good yields were obtained from the untreated Solka-floc samples SW-40 and BW-200 (samples 8 and 9).

The best yields were obtained from those samples which were treated with 10 percent sodium hydroxide, either with (sample 6) or without (sample 7) ultraviolet irradiation. Similarly, improved yields were obtained from ball-milled BW-200 Solka-floc which had been subjected to no other treatment. The Klett turbidities in these cases ranged from 810 to 880, the highest obtained in these experiments. The beneficial effect of the alkali treatment is consistent with the finding of Callihan and Dunlap[3]. The improved yields due to the ball-milling, and also the alkali treatments, may be due to the reduction in crystallinity and the associated increase in accessibility[12,34,35]. Though the particle size was not characterized here, comparing Figure 9 with Figure 11 clearly shows that the ball-milling had effected a marked reduction in particle size.

In Table 22 it can again be seen that ball-milling enhanced the bacterial yield (samples 1 and 2); ultraviolet irradiation in this case was without effect. Almost as good a yield was obtained from a slurry in 1 percent sodium nitrite which was stirred for 19 hours, without irradiation, at 50°C, the temperature achieved by those reaction mixtures which were irradiated.

The lowest yield in Table 22 is that obtained from sample 4, in which a sample of Solka-floc was made up as a 10 percent slurry in water, with no

sodium nitrite and without irradiation. However, the last three samples in Table 22, which were obtained from Solka-floc which was irradiated as 2.7 percent slurries in 1 percent sodium nitrite for 2, 6, and 19 hours, show that short-time irradiations result in moderate bacterial yields, the yields decreasing with increasing irradiation time. The latter effect is qualitatively consistent with the finding shown in Table 21 and mentioned above; namely, that 19 hours irradiation resulted in greater yields than did 48 hours.

The major conclusions to be drawn from Tables 20, 21, and 22 may be summarized as follows: the best treatments for promoting the growth of Alcaligenes faecalis-Cellulomonas, sp., mixed cultures on cellulose are comminution of the cellulose to small particle size, and treatment of the cellulose with 10 percent sodium hydroxide. While ultraviolet irradiation, with or without nitrite, is not a practical pretreatment, chemical pretreatments which can produce similar changes at lower cost appear worthy of investigation.

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APPENDIX

MATERIALS AND METHODS

A. Materials

1. Substrates.

a. Cotton Linters paper. This paper was filter paper No. 049 manufactured from chlorine bleached cotton linters by the Eaton-Dikeman Company, Mount Holly Springs, Pennsylvania[a]. It had a thickness of about 0.007 inch and a basis weight (weight of 500 sheets, each 20 in. by 20 in.) of 25 pounds. It was stated to be more than 99 percent alpha-cellulose.

b. Purified Wood Cellulose. This material, Solka-floc, made by the Brown Company, Milton Village, Massachusetts, was a finely divided wood pulp cellulose comprising at least 99.5 percent alpha-cellulose. Two grades were used in this work, the Solka Floc SW-40 and the Solka Floc BW-200. According to the manufacturer's literature the particle size of the SW-40 was such that 1 percent remained on a 40-mesh screen, 59 percent passed a 100-mesh screen, and 32 percent passed a 200-mesh screen; the average particle size was 100 microns long by 16 microns diameter. In the case of the BW-200, 1 percent remained on a 40-mesh screen, 96.5 percent passed a 100-mesh screen, and 83% passed a 200-mesh screen; its average particle size was 50 microns long by 17 microns diameter.

2. Chemicals and Reagents.

a. Cadoxene. This reagent is an aqueous alkaline solution of cadmium (II) hydroxide tris(ethylenediamine). It is a cellulose solvent, and was employed

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a. Trade names are given as part of exact experimental conditions, and are not to be construed as an endorsement of the named products over equivalent ones of other manufacturers.

in the determination of the degree of polymerization by viscometric methods. The reagent was prepared according to the method given by Brown[36].

b. Potassium ferrioxalate. This compound was employed as a chemical actinometer. It was prepared as described by Hatchard and Parker[37] using reagent grade chemicals.

c. Deuterium oxide. This material employed in the determination of the crystallinity of cellulose was obtained from Ventron Corporation, Alfa Products, Beverly, Massachusetts and was labelled as being 99.75 percent deuterium oxide. It was handled only in a dry environment to avoid pickup of atmospheric moisture.

d. Miscellaneous chemicals. Other chemicals, such as sodium nitrite, ferric chloride, and sodium hydroxide, were all reagent grade materials.

3. Equipment.

a. Photochemical Reactor. This reactor was a Rayonet Model RPR-100, obtained from the Southern New England Ultraviolet Company, Middletown, Connecticut. It consists of a sheet metal housing (see Figure 12) within which is a bank of 16 tubular ultraviolet lamps, each 28.5 cm (about 11 in.) long, mounted vertically around a circle of 23.5 cm (9.25 in.) diameter. Three sets of lamps are available, with spectral distributions peaking at 254 nm, 300 nm, and 350 nm, respectively. Surrounding this cylinder of lamps is a polished cylindrical reflector, 39 cm (15 in.) high by 26 cm (about 10 in.) diameter.

A fan in the base of the reactor blows air through the irradiation space, to cool the material being irradiated. For the experiments described in this report, a magnetic stirrer switched from the outside was installed on the floor of the irradiation space so that the aqueous dispersions of cellulose could be stirred during irradiation. Figure 13 is a view of the interior of the reactor, showing the bank of lamps and the stirrer.

For irradiating dry paper samples, an accessory known as a "merry-go-round" sample holder was employed. This device, manufactured by the Southern New England Ultraviolet Company, for use with the Model RPR-100 Reactor, is shown in Figure 12 to the right of the reactor. It consists of a 5-rpm motor, mounted with its 34.4 cm (12 in.) long shaft vertical. Held on the shaft by means of detent clips are two parallel discs, whose distance apart is adjustable. As employed in this work, paper strips were mounted between the upper and lower discs, the mounting centers being 8.3 cm (3.25 in.) from the merry-go-round axis. The plane of the paper was perpendicular to the radius of the reactor. With the merry-go-round in the reactor, the paper strips moved around a circle about 2.5 cm (1 in.) inside the circle of lamps.

For irradiating cellulose suspensions, cylindrical quartz tubes with round bottoms were employed. The one used most frequently had an inside diameter of 5.1 cm, a wall thickness of 1.8 mm, and an overall length, exclusive of the 24/40 standard taper opening, of 33 cm. In use, it was mounted in the center of the illuminated space with its bottom resting on the magnetic stirrer; a stirrer bar in the tube permitted the contents to be stirred during the irradiation.

b. Spectrophotometers. Three spectrophotometers were employed for various analytical tasks in connection with the work described herein. These were the Perkin-Elmer Model 221G, an automatic scanning and recording infrared spectrophotometer, covering the range of wavenumbers from 500 to 4,000 cm^{-1}, the Perkin-Elmer Model 202, an automatic scanning and recording spectrophotometer in the ultraviolet and visible range from 350 to 750 nm, and the Beckman DU, an ultraviolet to the near infrared spectrophotometer, from 200 nm to 2,000 nm, featuring manual wavelength selection and visual read-out.

c. Dilution viscometer. This viscometer of the Cannon-Ubbelohde type, size 75, was made by the Cannon Instrument Company, State College, Pennsylvania.

B. Methods

1. Treatment of Substrates with Soluble Salts

a. Paper Strips. The cotton linters paper was irradiated in the air-dried condition. The paper was cut into 2.54 cm (1 in.) by 15.24 cm (6 in.) strips. The average weight of each strip, after air-drying, was 0.3131g, with a 95 percent confidence interval of 0.0025g. To achieve a 1 percent add-on of sodium nitrite, each strip of paper was treated with 0.36 ml of a solution containing 8.75g per liter of sodium nitrite. The solution was applied dropwise from a 1 ml hypodermic syringe through a number 26 needle. The droplets were applied sufficiently close together so that as each drop spread in the paper its field overlapped those of adjacent drops. The paper appeared uniformly wet after the required quantity of solution had been added, and there was no tendency for the paper to drip when hung to air dry. It generally required about 33 drops to cover a 2.54 cm (1 in.) by 15.24 cm (6 in.) strip.

Add-ons of 0.1 percent and 10 percent sodium nitrite were obtained in a similar manner. The volume added was kept at 0.36 ml, but the solution concentrations employed were 0.875g per liter and 87.5g per liter, respectively.

The paper strips were treated with ferric chloride in the same way, except that the amounts added were 0.05 percent, 0.2 percent, and 1 percent, requiring ferric chloride solution concentrations of 0.4375g per liter, 1.75g per liter, and 8.75g per liter, respectively.

b. Cellulose Powders. In the case of the cotton linters paper, the paper was first pulped in an Osterizer in the presence of the desired amount of sodium nitrite solution. The resulting slurry was transferred to the 5.1 cm diameter quartz tube for irradiation in the reactor.

Since Solka-floc was supplied as a powder, no pulping was necessary with this material. It was prepared for irradiation by adding the required amount to the quartz tube, followed by the sodium nitrite solution, together with a stirrer bar for the magnetic stirrer. It was agitated for about five minutes with a magnetic stirrer, outside the photochemical reactor, in order to insure good dispersion of the powder.

2. Ultraviolet Irradiation. As described in the Equipment section above, the irradiations were carried out in the photochemical reactor. Slurries were irradiated in the 5.1 cm quartz tube, mounted in the center of the irradiated volume, whereas paper strips were irradiated on the merry-go-round, which could accomodate eight strips at a time.

3. Determination of Degree of Polymerization. The degree of polymerization (DP) was calculated from the intrinsic viscosity, which was determined using the method described by Swenson[38]. Solutions of the cellulose substrates in cadoxene reagent were prepared by dissolving about 50 mg (carefully weighed) of cellulose in the reagent cooled in an ice bath, then making up to 10.00 ml. An 8-ml aliquot of this solution was diluted with an equal volume of water, then 10.00 ml of this diluted solution was charged into the viscometer, and the viscosity determined. The material in the viscometer was then diluted with 5 ml, then 10 ml, then another 10 ml, of 1:1 cadoxene reagent (previously prepared by diluting the stock cadoxene with water), the viscosity being determined after each addition of 1:1 cadoxene. From these data, the intrinsic viscosity, the DP, and the average molecular weight were calculated[38,39,40]. Further, from the DP obtained for the partially degraded cellulose, the average number of scissions needed to reduce the original DP to that found for the treated material was calculated[27]. The equations for these calculations are given by Swenson[38], and in references 27, 39 and 40.

4. Actinometry. The procedure employed was that of Hatchard and Parker[37]; it is described in detail by Calvert and Pitts[41]. It is based on the photochemical reduction of the iron (III) in acidified potassium ferrioxalate solutions to iron (II), with the simultaneous oxidation of the oxalate; the iron (II) is then assayed spectrophotometrically after conversion to the red 1,10-phenanthroline complex, which has an absorption maximum at 510 nm.

In studying the intensity of radiation in the Rayonet reactor, measurements were made in the center, and in one of the eight equivalent merry-go-round positions used for the paper strips. For the center, 125 ml of a solution that was 0.006M in potassium ferrioxalate and 0.01N in sulfuric acid was charged into the 5.1 cm diameter quartz tube, with a magnetic stirrer bar, and placed in the center of the irradiated space. This volume of solution had approximately the same area of irradiated vertical surface as the vigorously stirred cellulose slurries; the resulting measurement thus represented the actual amount of radiation which would be experienced by the cellulose slurry.

For measurements on the merry-go-round, a 1.3 cm diameter quartz tube was employed, and was charged with 17 ml of the ferrioxalate solution, which filled the tube to a height of 12.6 cm.

It was found that if the center position was irradiated for 60 seconds and the merry-go-round position for 24 seconds (i.e., two revolutions of the merry-go-round) the amount of iron (III) reduced to iron (II) was 17 percent of that available. This was the maximum extent of reduction permitted in order to ensure linearity of response. Thus, the center position was irradiated for 30 seconds and for 60 seconds, in replicate determinations, while the merry-go-round position was irradiated for 12 seconds and 24 seconds. These gave amounts of iron (II) which minimized experimental errors; this was demonstrated by the good agreement among the replicates.

The Beer's Law curve for the spectrophotometric determination of iron (II) was established using ferrous sulfate solutions titrated with standard potassium permanganate. The curve is shown in Figure 14.

The quantum efficiency of the reduction of iron (III) to iron (II) in potassium ferrioxalate has been determined at various wavelengths by Hatchard and Parker[37]. Thus, knowing the amount of iron (II) formed in a given irradiation for a given amount of time, the number of quanta per unit volume of actinometer solution per unit time could be calculated. Clearly, this would be the same radiation intensity experienced by an equal volume of any other material with the same geometry, e.g., a cellulose slurry being irradiated. The equations for these calculations are given by Calvert and Pitts[41].

5. Determination of Nitrite. Nitrite was determined by the method of Hartley and Asai[29]. In this method, the reaction of nitrite and 2,6-xylenol in strong acid medium to yield 4-nitroso-2,6-xylenol as the major product is used. Though the yield is not 100%, the fraction produced is sufficiently reproducible if the preparative conditions for the sample are carefully controlled. The 4-nitroso-2,6-xylenol is determined spectrophotometrically at 306 nm. The calibration curve determined from solutions of sodium nitrite of known concentration is shown in Figure 15.

6. Determination of Accessibility to Water. The method employed here is described by Mann and Sharples[42]. It relies on the fact that when cellulose is immersed in deuterium oxide, deuterium is exchanged for hydrogen in the cellulose hydroxyl groups, the exchange being more rapid in the amorphous regions of the cellulose, which are more accessible than in the crystalline regions. Thus, if an excess of deuterium oxide is employed and the contact time is limited, the exchanged hydrogen, which appears as hydrogen deuterium oxide (HDO) in the reaction medium, will be mainly from the amorphous

regions[30,32,43,44,45]. The amount of HDO is then determined by infrared (IR) spectrophotometry, measuring the intensity of the -OH stretching band at 3400 cm^{-1}, after first calibrating the spectrophotometer with D_2O-H_2O mixtures. (At low H_2O concentrations in these calibrating mixtures, the added H_2O will be converted almost quantitatively to HDO.)

In this work, the cellulose sample was charged into a flask, whose dry weight was determined after an overnight pumping to remove adsorbed water. The flask was fitted with an adaptor bearing a stopcock, permitting it to be removed from the vacuum system without exposing the contents to the atmosphere. The sample was dried to constant weight by pumping at 60°C. The quantity of sample selected usually weighed from 2.5g to 3.0g when dry.

A measured quantity of between 10 ml and 15 ml of deuterium oxide was added to the cellulose in the flask in a glove bag, filled with dry nitrogen and which contained a dish of magnesium perchlorate to further insure dryness. The hypodermic syringes and needles employed in the liquid transfers were dismantled and stored in the glove bag for at least three hours prior to their use. The mixture of cellulose and deuterium oxide in the stoppered flask was left to stand for four hours for the exchange to take place.

The flask with the reaction mixture was then attached to the vacuum system, the contents frozen with liquid nitrogen, and the system pumped down. A receiver, bearing an adaptor with a stopcock, was also attached to the vacuum system and simultaneously pumped down. When the minimum pressure of about one to two millitorr had been reached, the flask and receiver were isolated from the pump, the receiver was cooled with liquid nitrogen and the reaction flask permitted to warm to room temperature. The liquid in the reaction flask thereby distilled into the receiver and the distillation was generally continued until about one to five ml had been collected for analysis.

Because of the very high IR absorption of H_2O and D_2O, cells of very short path length were employed. The cells used had Irtran windows and path lengths of 26 to 27 micrometers. Since the two cells employed differed by about one micrometer in path length, the same cells were always employed for the reference liquid and sample, respectively.

The calibrating solutions ranged in composition from 1 percent to 4.5 percent water in D_2O; these solutions were made up and handled in the glove bag, to avoid contamination by atmospheric moisture. The calibration curve is shown in Figure 16.

TABLE 1

RADIATION INTENSITIES IN THE RAYONET REACTOR

Location	quanta/ml-sec at: 254 nm	300 nm	350 nm
Center position[a]	6.5×10^{15}	6.0×10^{15}	8.2×10^{15}
Merry-go-round position[b]	2.0×10^{16}	2.1×10^{16}	2.6×10^{16}

a. 125 ml of actinometer solution in a 5.1 cm diameter quartz tube.

b. 17 ml of actinometer solution in a 1.3 cm diameter quartz tube.

TABLE 2

DEGREE OF POLYMERIZATION OF SW-40 SOLKA-FLOC SLURRIES IN SODIUM NITRITE SOLUTIONS AFTER IRRADIATION AT 254 NM

Conc. $NaNO_2$, % \ irrad. time, hr.	2.7% slurry[a]			1.5% slurry[b]		
	0	6	19	2	7	27
0	1100	660	400	780	510	280
1	----	610	290	790	460	150
10	----	710	400	850	530	260

a. 3.5g Solka-floc in 130 ml of H_2O or $NaNO_2$ solution.

b. 1.5g Solka-floc in 100 ml of H_2O or $NaNO_2$ solution.

TABLE 3

DEGREE OF POLYMERIZATION OF SW-40 AND BW-200 SOLKA-FLOC SLURRIES[a] IN DILUTE SODIUM NITRITE SOLUTIONS AFTER IRRADIATION FOR 19 HOURS AT 254 NM

Conc. $NaNO_2$ (%)	DP	
	SW-40	BW-200
0	400	260
0.03	---	280
0.1	330	240
1.0	290	230

a. 3.5g Solka-floc in 130 ml of H_2O or $NaNO_2$ solution, yielding a 2.7% slurry.

TABLE 4

DEGREE OF POLYMERIZATION OF BW-200 SOLKA-FLOC
IRRADIATED FOR VARIOUS TIMES AT 254 NM
AS 10 PERCENT SLURRIES[a] IN DILUTE
SODIUM NITRITE SOLUTIONS

Conc. $NaNO_2$ (%)	19-hr irradiation		48-hr irradiation	
	DP	no of scissions	DP	no of scissions
0	430	2.9	230	7.0
0.1	430	2.9	300	5.0
1.0	300	5.0	150	11.3

a. 10g Solka-floc in 100ml of H_2O or $NaNO_2$ solution.

TABLE 5

EFFECT OF SLURRY CONCENTRATION OF BW-200 SOLKA-FLOC IN DILUTE SODIUM NITRITE SOLUTIONS UPON DEGREE OF POLYMERIZATION FOLLOWING 19 HOURS' IRRADIATION AT 254 NM

Conc. $NaNO_2$ (%)	DP	
	2.7% slurry[a]	10% slurry[b]
0	260	430
0.1	240	430
1.0	230	300

a. 3.5g Solka-floc in 130 ml of H_2O or $NaNO_2$ solution.

b. 10g Solka-floc in 100 ml of H_2O or $NaNO_2$ solution.

TABLE 6

EFFECT OF WAVELENGTH ON THE DEGREE OF POLYMERIZATION OF IRRADIATING 2.7 PERCENT SLURRIES[a] OF SW-40 SOLKA-FLOC IN SODIUM NITRITE SOLUTIONS IRRADIATED FOR 19 HOURS

Conc. $NaNO_2$ (%)	DP at: 254 nm	300 nm	350 nm
0	400	490	730
1	290	540	540
10	400	580	---

a. 3.5g Solka-floc in 130 ml of H_2O or $NaNO_2$ solution.

TABLE 7

pH OF FILTRATES FROM THE IRRADIATION OF 1.5 PERCENT SLURRIES[a] OF SW-40 SOLKA-FLOC IN SODIUM NITRITE SOLUTIONS AT 254 NM

Conc. $NaNO_2$ (%)	pH after irradiating for: 0 hr	2 hr	7 hr	27 hr
0	5.3	6.3	3.8	3.5
1	5.8	6.4	6.1	5.2
10	6.4	7.1	6.9	6.8

a. 1.5g Solka-floc in 100 ml of H_2O or $NaNO_2$ solutions.

TABLE 8

pH OF SOLKA-FLOC SLURRIES[a] TO WHICH 1N SULFURIC ACID WAS ADDED

Conc. $NaNO_2$ (%)	Initial pH	pH after addition of 1N H_2SO_4: 1 ml	2 ml
0	5.3	2.5	2.2
1	5.6	4.7	4.0

a. 10g BW-200 Solka-floc in 100ml H_2O or $NaNO_2$ solution.

TABLE 9

pH OF FILTRATES FROM SOLKA-FLOC SLURRIES
WHICH HAD LITTLE OR NO IRRADIATION

Slurry conc. (%)	Sodium nitrite conc. (%)	Irradiation[a] time (hr)	pH	
			Initial	Final
2.7[b]	1	1	5.6	6.3
2.7[b]	1	0.5	5.6	5.9
10 [c]	0	None[d]	5.3	6.3

a. 254 nm.

b. 4.0g BW-200 Solka-floc in 148ml 1% $NaNO_2$ solution.

c. 10g BW-200 Solka-floc in 100ml H_2O.

d. No irradiation; 4 hr stirring at room temperature.

TABLE 10

IRRADIATION[a] OF SOLKA-FLOC SLURRIES[b] TO WHICH VARIOUS AMOUNTS OF SULFURIC ACID OR SODIUM HYDROXIDE HAD BEEN ADDED

Additive[d]	Amount (%)	0% $NaNO_2$ pH Before irrad	0% $NaNO_2$ pH After irrad[c]	0% $NaNO_2$ DP	1% $NaNO_2$ pH Before irrad	1% $NaNO_2$ pH After irrad[c]	1% $NaNO_2$ DP
H_2SO_4	0	5.3	3.6	430	5.6	5.5	300
H_2SO_4	0.05	2.5	2.5	340	4.7	5.0	190
H_2SO_4	0.1	2.2	2.2	330	4.0	4.5	160
H_2SO_4	0.15	---	---	---	3.8	4.7	150
NaOH	0.08	---	---	---	11.4	7.0	330

a. 254 nm for 19 hours.

b. 10g BW-200 Solka-floc in 100ml H_2O or 1% $NaNO_2$ solution.

c. pH of the filtrate.

d. The additive was 1N acid or alkali.

TABLE 11

IRRADIATION[a] OF 10 PERCENT BW-200 SOLKA-FLOC SLURRIES[b] IN 1 PERCENT SODIUM NITRITE, WITH AND WITHOUT ADDED SULFURIC ACID, IN OXYGEN OR NITROGEN ATMOSPHERES

Amount H_2SO_4 (%)	O_2 Atmosphere[c]		N_2 Atmosphere[c]	
	Filtrate pH	DP	Filtrate pH	DP
0	5.1	280	9.5	390
0.1	2.3	220	8.8	270

a. 254 nm for 19 hours.

b. 10g Solka-floc in 100 ml of 1% $NaNO_2$.

c. Gas bubbled vigorously through mixture for 15 minutes, then at the rate of 10-15 ml per minute during the irradiation.

TABLE 12

IRRADIATION OF 0.25 PERCENT SODIUM NITRITE SOLUTION IN WATER WITH 254 NM RADIATION

Sample no.	Cumulative irradiation time (hr)	pH	Amount $NaNO_2$ (%)
1	0	6.7	0.26
2	2.3	6.9	0.27
3	4.4	6.8	0.25
4	21.9	6.7	0.24

TABLE 13

ANALYSIS FOR NITRITE OF FILTRATES FROM IRRADIATED SLURRIES[a] WITH VARIOUS ADDITIVES AND ATMOSPHERES

Additive; Atmosphere	Conc. $NaNO_2$ remaining (%)	Filtrate pH	DP of cellulose	No. of scissions per molecule	Molecules $NaNO_2$ consumed per scission
0.1% H_2SO_4; still air	0.13	4.5	160	10.4	18.3
0.1% H_2SO_4; O_2	0.12	2.3	220	7.1	27.0
0.1% H_2SO_4; N_2	0.65	8.8	270	5.5	13.9
None; still air	0.68	5.5	300	4.9	14.2
None; O_2	0.64	5.1	280	5.3	14.8
None; N_2	0.87	9.5	390	3.3	8.6

a. 10g BW-200 Solka-floc in 100 ml of 1% $NaNO_2$ solution, with the indicated additive. Irradiated for 19 hours at 254 nm.

TABLE 14

ABSORPTION AT SELECTED WAVELENGTHS OF FILTRATES FROM 2.7 PERCENT SW-40 SOLKA-FLOC SLURRIES FOLLOWING IRRADIATION FOR 19 HOURS

Solution No.	Initial Concentration $NaNO_2$ (%)	Wavelength (nm)	Absorbance at: 254 nm	300 nm	350 nm
1[a]	1	---	1.66	1.20	2.99
2[a]	10	---	>3.00	>3.00	>3.00
3	1	254	1.75	1.25	2.67
4	10	254	>3.00	>3.00	>3.00
5	1	300	1.78	1.27	2.89
6	10	300	>3.00	>3.00	>3.00
7[b]	10	254	1.71	1.24	sl. >3.00
8[c]	10	300	1.67	1.21	2.98
9	0	254	0.10	0.04	0.01
10	0	300	0.14	0.09	0.05

a. Control solution. Contained only $NaNO_2$ (no cellulose) and was not irradiated.

b. Solution 4, diluted 1:10 with water.

c. Solution 6, diluted 1:10 with water.

TABLE 15

APPARENT QUANTUM EFFICIENCIES IN THE IRRADIATION AT 254 NM OF COTTON LINTERS PAPER STRIPS WITH 1 PERCENT SODIUM NITRITE ADD-ON

Irradiation time (hr)	DP	No. of scissions per molecule	Quanta[a] per scission
0.5	340	5.8	120
1	320	6.3	220
3	240	8.9	460
8	210	10.1	1100
24	180	12.2	2700

a. The energy values for the flat paper strips were calculated from the values in Table 1 for the 1.3 cm quartz tube in the merry-go-round position. The assumption was made that the energy required to affect the actinometer solution entered the tube through the peripheral area of the cylindrical volume comprising the actinometer solution, thus enabling the calculation of the energy in terms of quanta per cm^2.

TABLE 16

APPARENT QUANTUM EFFICIENCIES IN THE IRRADIATION AT 254 NM OF SW-40 SOLKA-FLOC SLURRIES IN 1 PERCENT SODIUM NITRITE SOLUTIONS

Irradiation time (hr)	1.5% Slurry		2.7% Slurry	
	No. of scissions	Quanta per scission	No. of scissions	Quanta per scission
2	1.4	830	---	---
6	----	----	2.1	860
7	3.5	1160	2.2	950
19	----	----	6.5	890
27	13.7	1150	---	---

TABLE 17

APPARENT QUANTUM EFFICIENCIES IN THE IRRADIATION AT 254 NM OF 2.7 PERCENT SLURRIES OF BW-200 SOLKA-FLOC IN 1 PERCENT SODIUM NITRITE SOLUTIONS

Irradiation time (hr)	No. of scissions	Quanta per scission
2	0.9	710
6	3.0	610
19	6.8	850
48	14.0	1110

TABLE 18

APPARENT QUANTUM EFFICIENCIES IN THE IRRADIATION AT 254 NM OF 10 PERCENT SLURRIES OF BW-200 SOLKA-FLOC IN SODIUM NITRITE SOLUTIONS OF VARIOUS CONCENTRATIONS

Irradiation time (hr)	0% $NaNO_2$		0.1% $NaNO_2$		1% $NaNO_2$	
	No. of scissions	Quanta per scission	No. of scissions	Quanta per scission	No. of scissions	Quanta per scission
19	2.9	570	2.9	570	4.9	340
48	7.0	600	5.0	840	11.3	370
19	---	---	---	---	11.3[a]	150[a]

a. This reaction mixture contained 0.15% H_2SO_4 in addition to the $NaNO_2$.

TABLE 19

ACCESSIBILITY TO AQUEOUS REAGENTS OF SEVERAL CELLULOSIC MATERIALS AS DETERMINED BY HYDROGEN-DEUTERIUM EXCHANGE IN LIQUID DEUTERIUM OXIDE

Material	Accessibility (%)
SW-40 Solka-floc	88
BW-200 Solka-floc	82
Cotton linters paper	66

TABLE 20

YIELD OF BACTERIA USING FILTER CAKES FROM ULTRAVIOLET-IRRADIATED BW-200 SOLKA-FLOC SLURRIES AS THE CARBON SOURCE

Sample No.	Amount $NaNO_2$(%)	Other Additives	Irrad. @ 254 nm (yes or no)	Reaction time (hr)	DP	Klett turbidity after 48 hrs[a]
1	0	0.05% H_2SO_4	yes	19	340	580
2	1	0.1% H_2SO_4	yes	19	160	410
3	0	0.1% H_2SO_4	yes	19	330	510
4	1	0.15% H_2SO_4	yes	19	150	388
5	1	O_2 gas	yes	19	280	480
6	1	0.1% H_2SO_4; O_2 gas	yes	19	220	550
7	1	N_2 gas	yes	19	390	410
8	1	0.1% H_2SO_4; N_2 gas	yes	19	270	400
9	1	---	no	6	880	410
10	1	---	no	19	810	440
11	0	---	no	4	950	420

a. Linearly related to the quantity of bacteria.

TABLE 21

YIELD OF BACTERIA USING FILTER CAKES FROM ULTRAVIOLET-IRRADIATED SOLKA-FLOC SLURRIES AS THE CARBON SOURCE

Sample No.	Amount $NaNO_2$ (%)	Other Additives	Irrad. @ 254 nm (yes or no)	Reaction time (hr)	DP	Klett turbidity after: 24 hr	48 hr
1	1	0.05% H_2SO_4	yes	19	190	330	640
2	0	---	yes	19	430	430	750
3	0	---	yes	48	230	380	700
4	1	---	yes	19	300	405	730
5	1	---	yes	48	150	350	660
6	1	10% NaOH	yes	19	----	375	880
7	1	10% NaOH	no	19	----	500	850
8	0	SW-40[a]	no	0	1100	350	700
9	0	BW-200[b]	no	0	930	375	730
10	0	Ball-milled BW-200[c]	no	0	----	590	810

a. SW-40 Solka-floc with no further treatment.

b. BW-200 Solka-floc with no further treatment.

c. Ball-milled BW-200 Solka-floc with no further treatment.

TABLE 22

YIELD OF BACTERIA USING ULTRAVIOLET-IRRADIATED SOLKA-FLOC SLURRIES AS THE CARBON SOURCE

Sample No.	Slurry[a] conc. for Irrad.(%)	Amount $NaNO_2$(%)	Irrad. @ 254 nm (yes or no)	Reaction time (hr)	Klett turbidity after: 24 hr	48 hr
1[b]	10	1	yes	19	550	750
2[b]	10	0	no	0	650	760
3[c]	10	1	no	19	530	700
4	10	0	no	0	230	250
5	2.7	1	yes	2	330	560
6	2.7	1	yes	6	320	520
7	2.7	1	yes	19	370	390

a. This is the concentration of the slurry employed in the indicated treatment. The sample slurries were all prepared from the washed, moist filter cakes and were 10 percent concentration in distilled water.

b. The cellulose was ball-milled BW-200 Solka-floc.

c. This slurry was stirred without irradiation for 19 hr at 50C, the temperature reached by those slurries which are irradiated in the photochemical reactor.

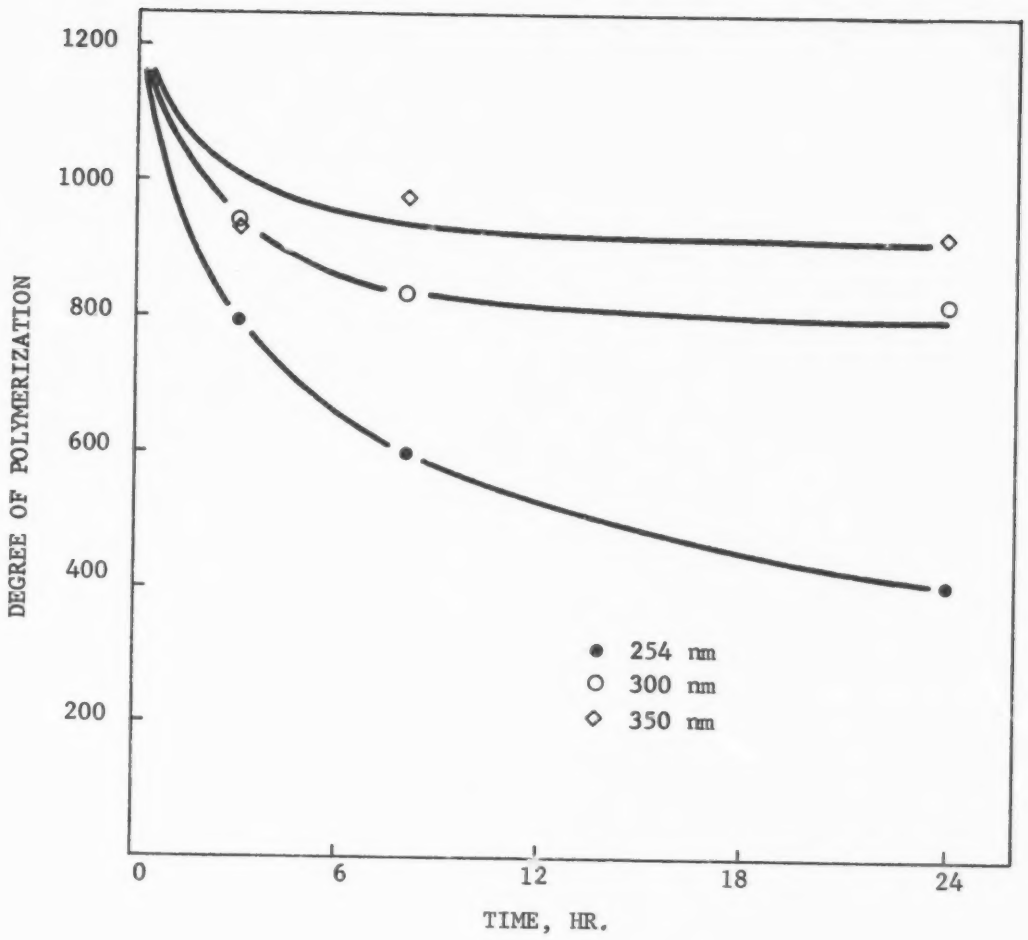

Figure 1. Effect of ultraviolet irradiation of various wavelengths on the degree of polymerization of untreated cotton linters paper.

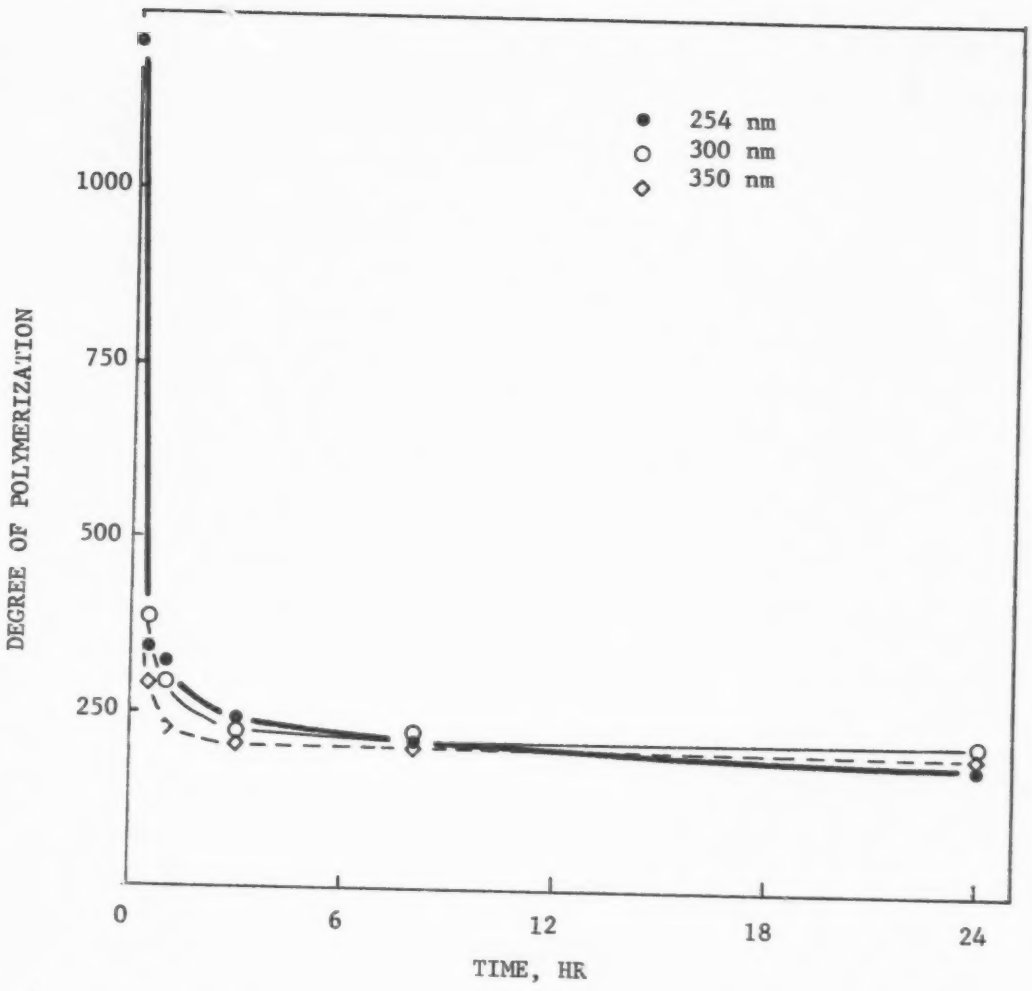

Figure 2. Effect of ultraviolet irradiation of various wavelengths on the degree of polymerization of sodium nitrite treated cotton linters paper.

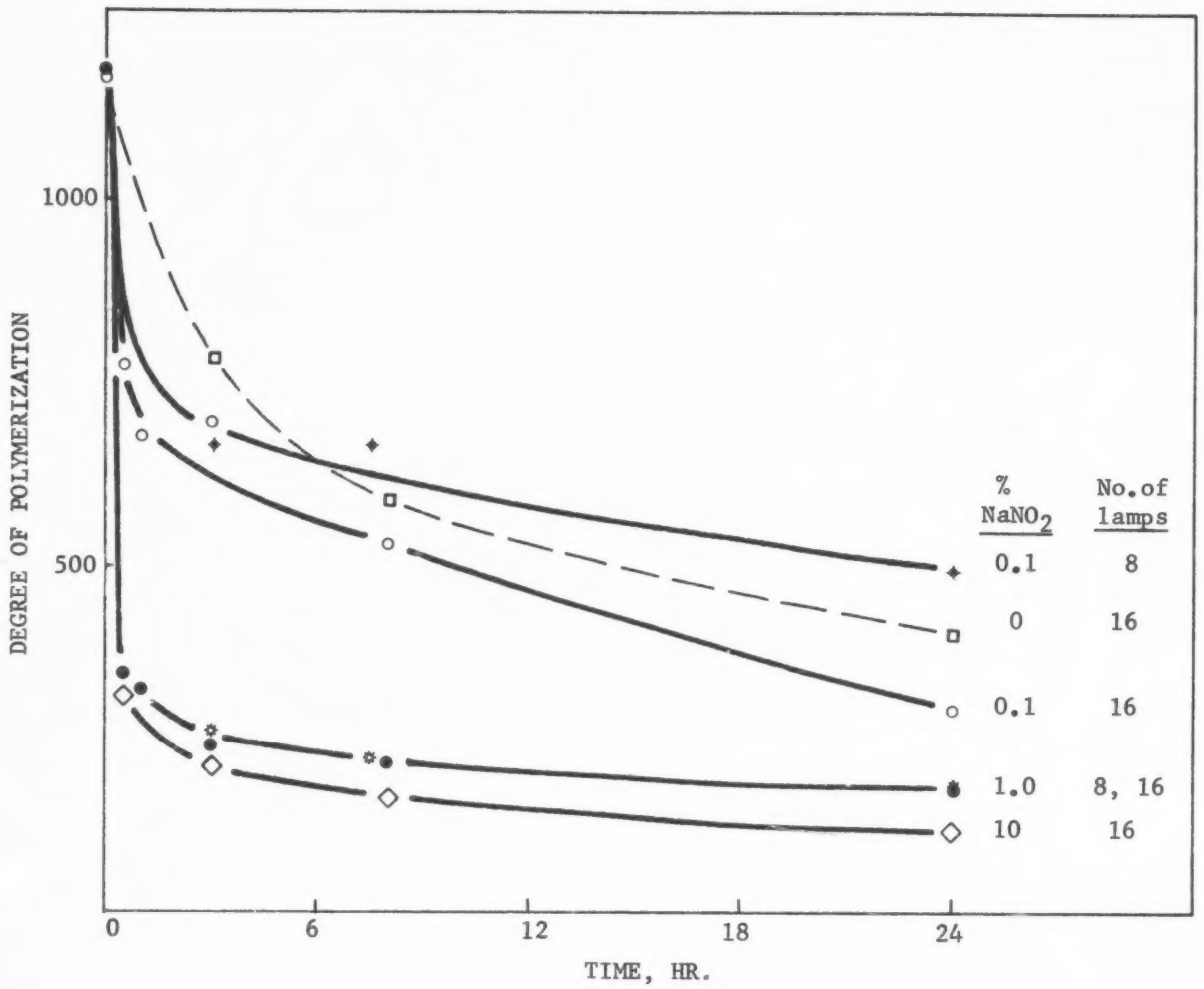

Figure 3. Effect of 254 nm radiation on sodium nitrite treated cotton linters paper.

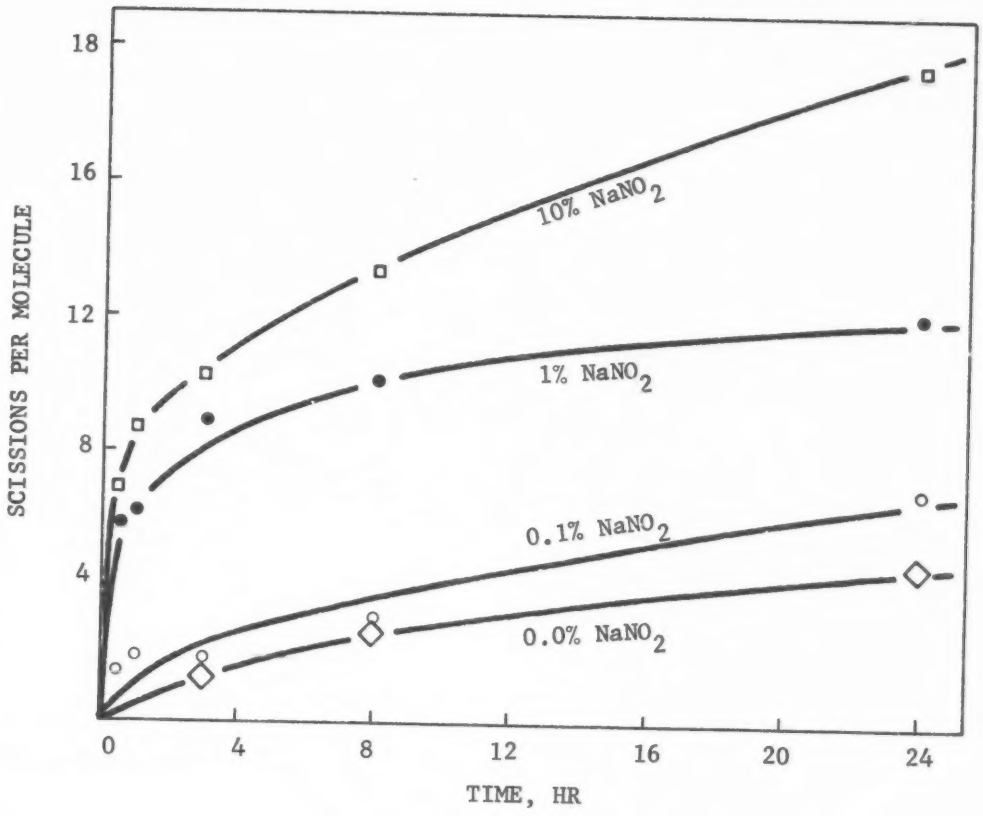

Figure 4. Effect of 254 nm radiation on the number of scissions per molecule for sodium nitrite treated cotton linters paper.

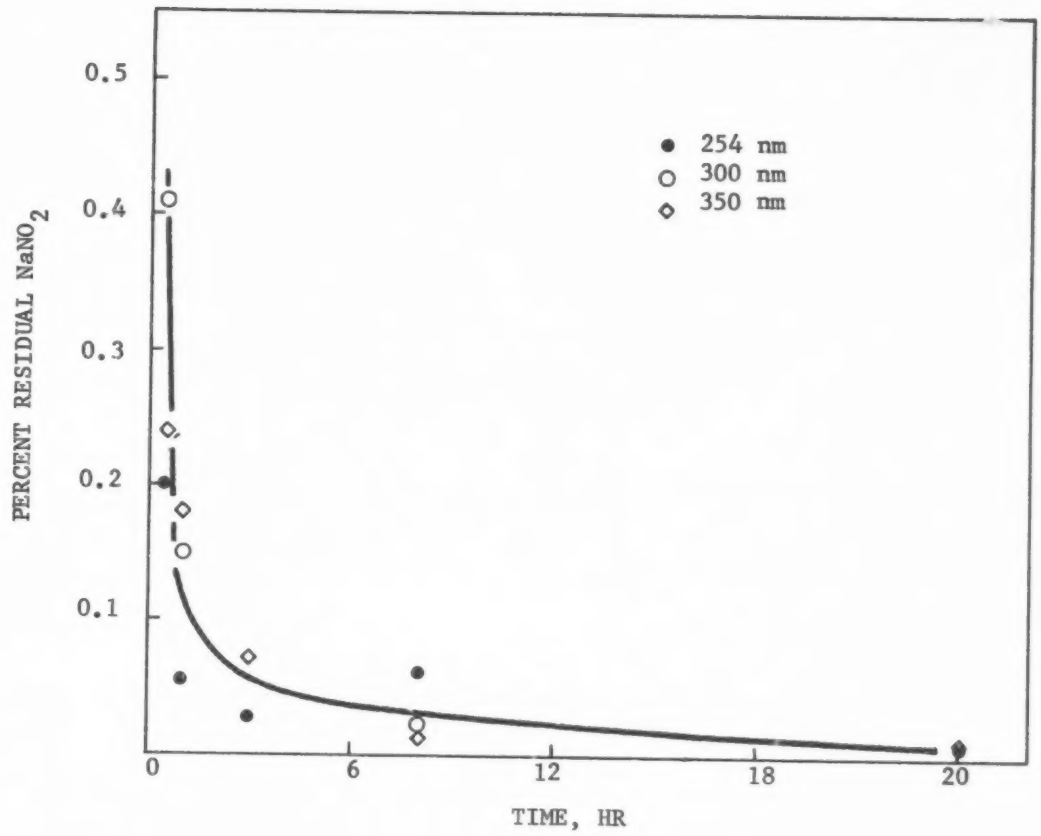

Figure 5. Depletion of sodium nitrite during irradiation of cotton linters paper originally containing 1% sodium nitrite.

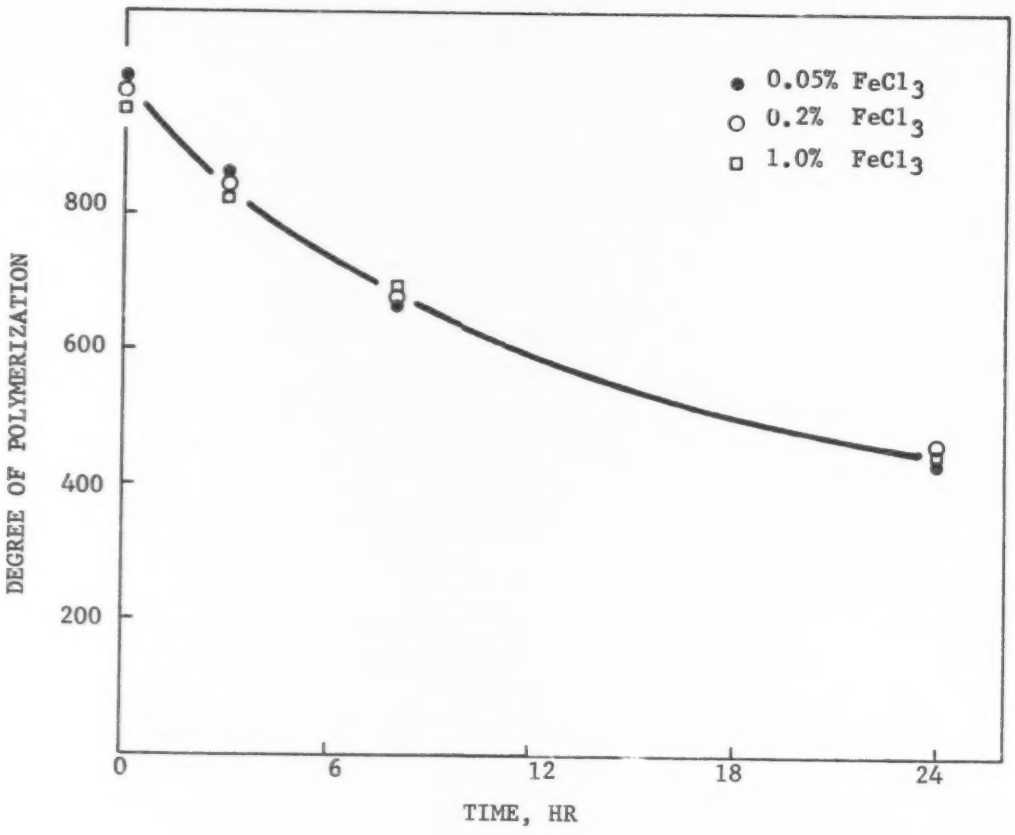

Figure 6. Effect of 254 nm irradiation on the degree of polymerization of ferric chloride treated cotton linters paper.

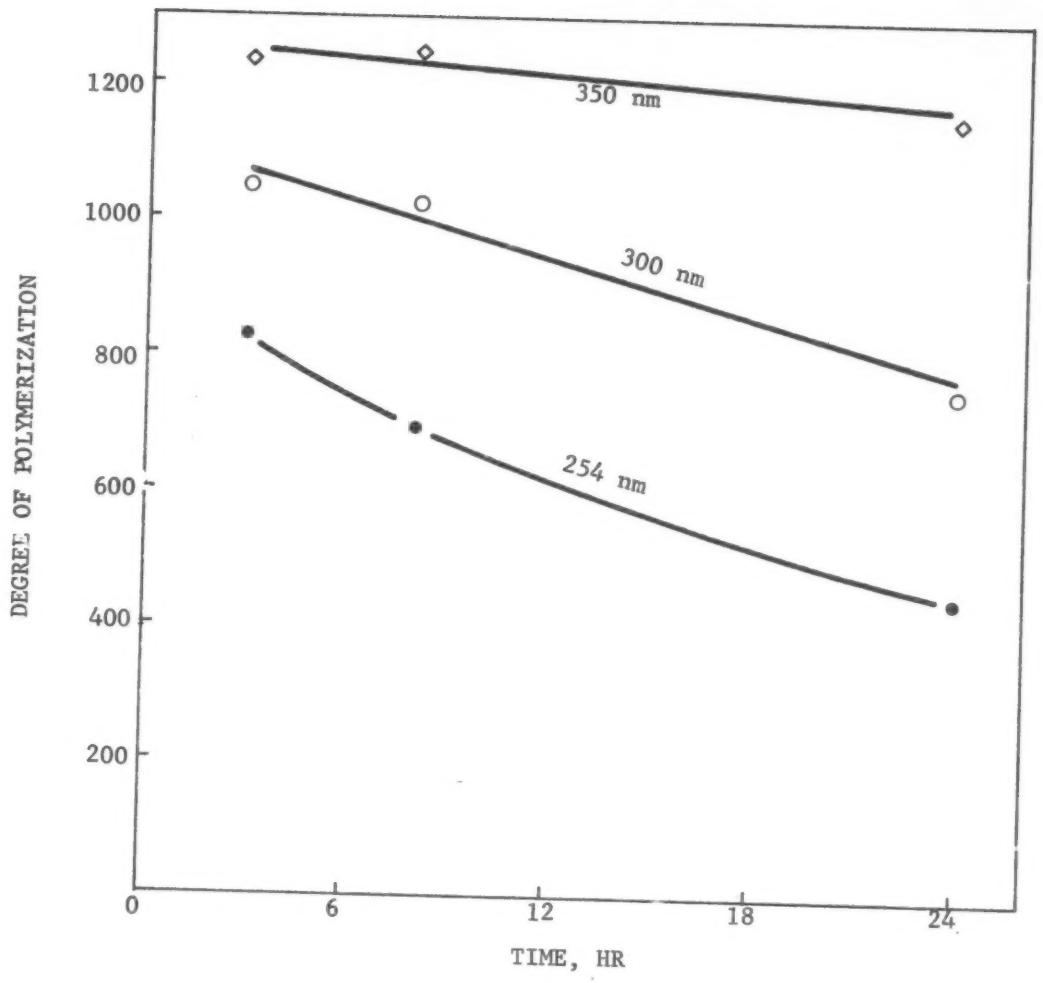

Figure 7. Effect of wavelength on the degree of polymerization of irradiated cotton linters paper containing 1% ferric chloride.

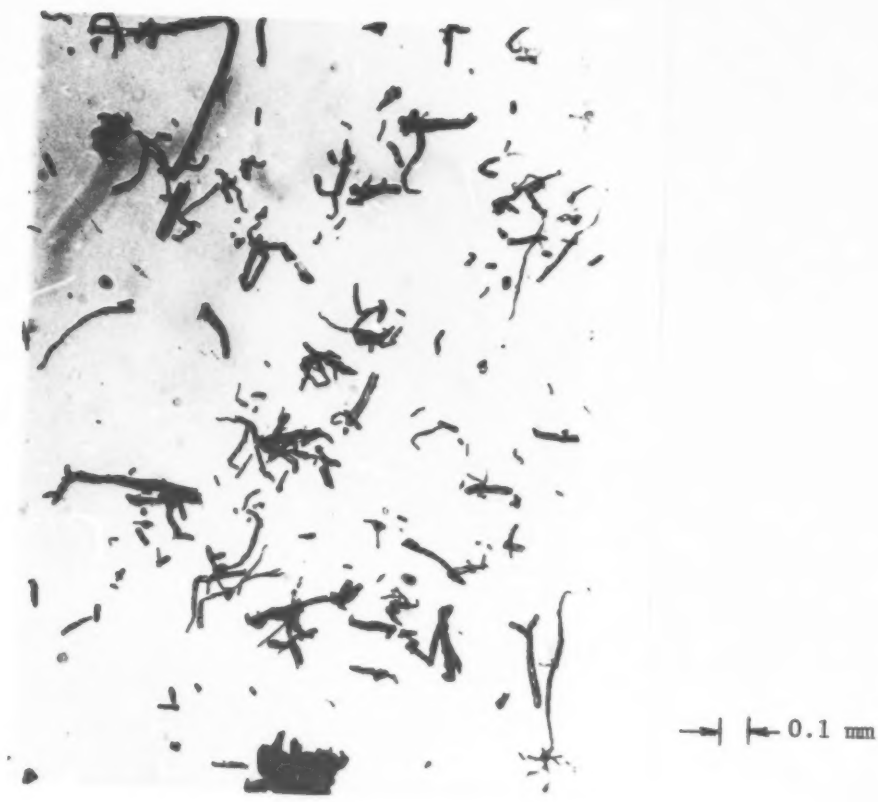

Figure 8 . Photomicrograph of SW-40 Solka-floc; transmitted light.

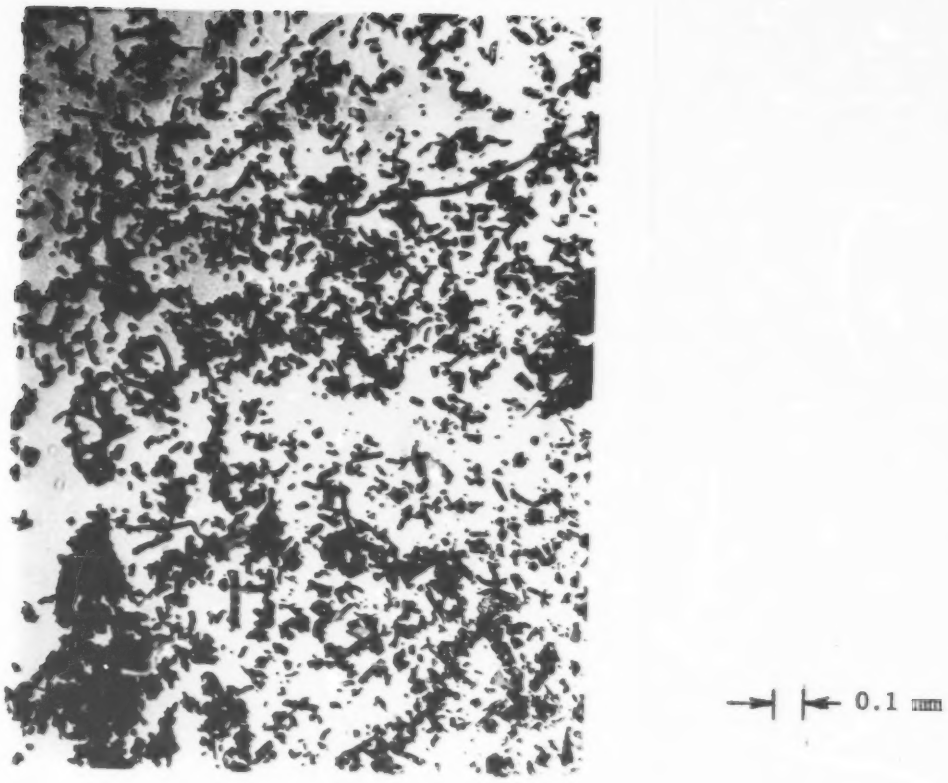

Figure 9. Photomicrograph of BW-200 Solka-floc; transmitted light.

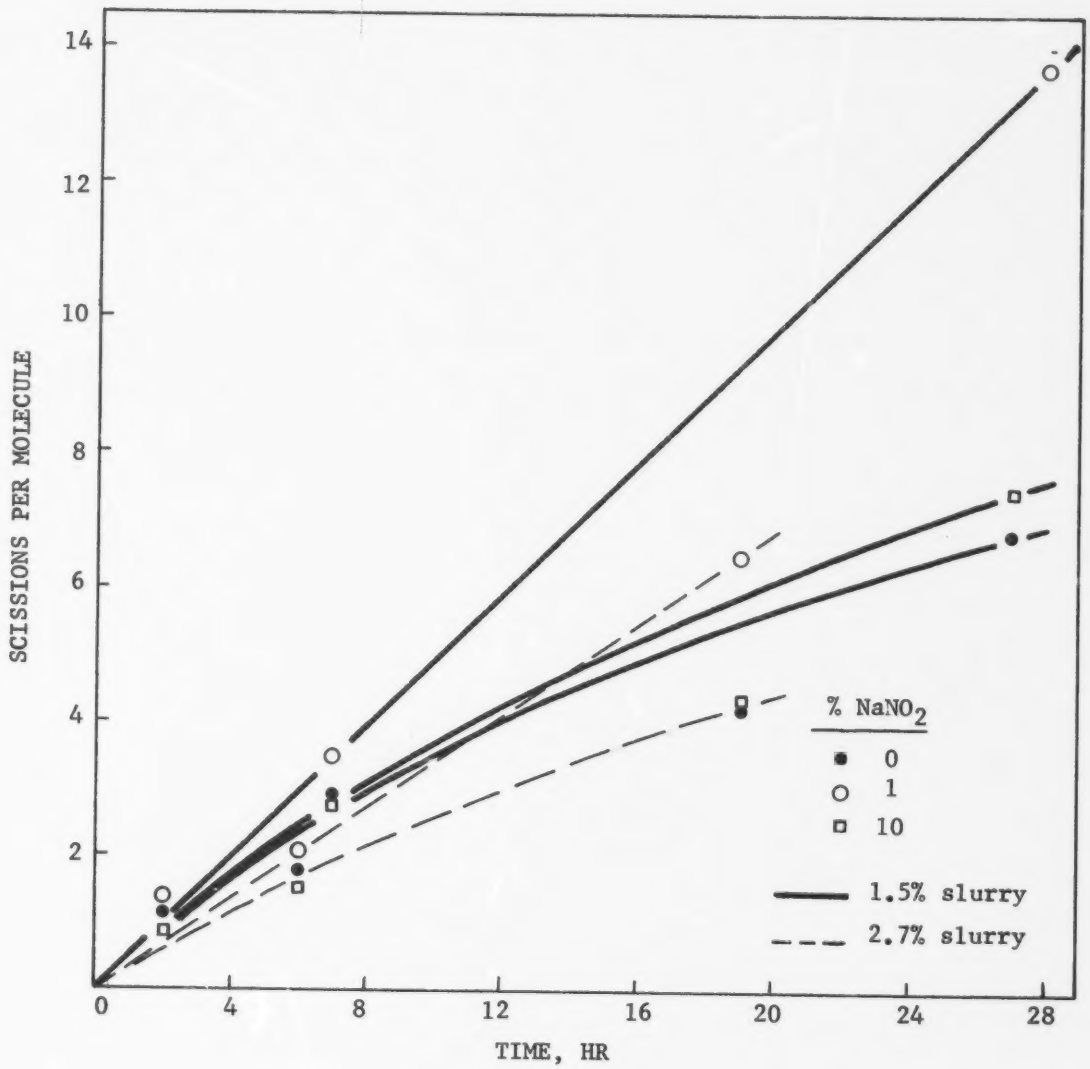

Figure 10. Effect of $NaNO_2$ concentration on the depolymerization of BW-40 Solka-floc slurries irradiated with 254 nm radiation.

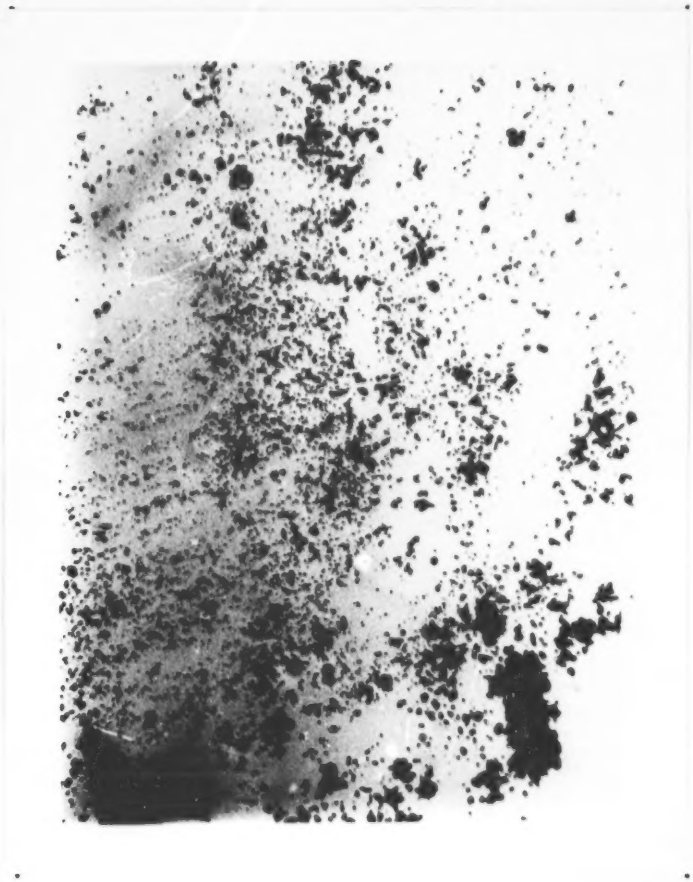

Figure 11. Photomicrograph of ball-milled BW-200 Solka-floc; transmitted light.

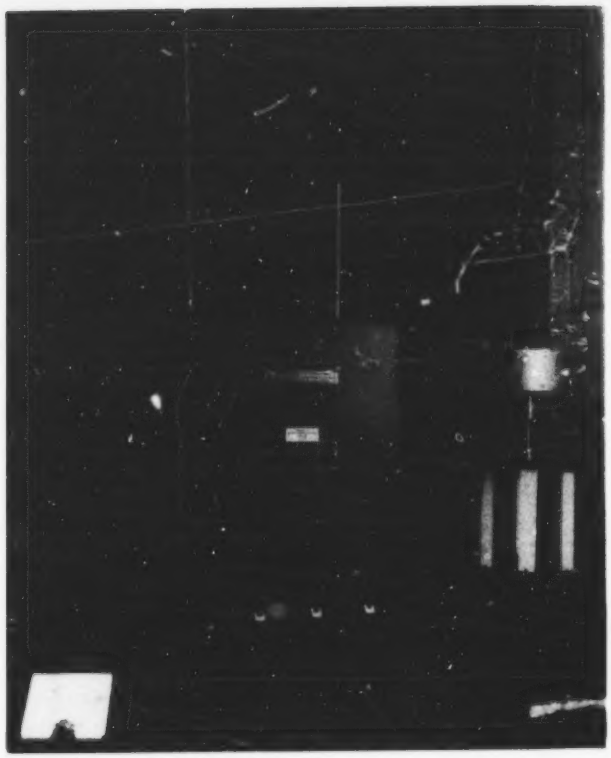

Figure 12. Photochemical reactor and "merry-go-round" sample holder. In the illustration the sample holder is loaded with paper strips, ready for irradiation. A quartz reaction tube, clamped to a support, is seen extending from the top of the reactor.

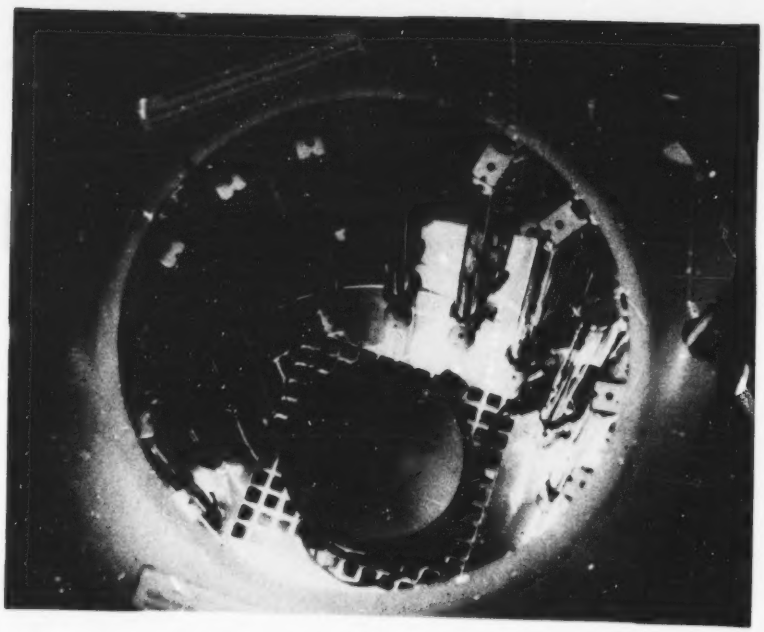

Figure 13. Interior of the photochemical reactor showing the bank of lamps and the magnetic stirrer.

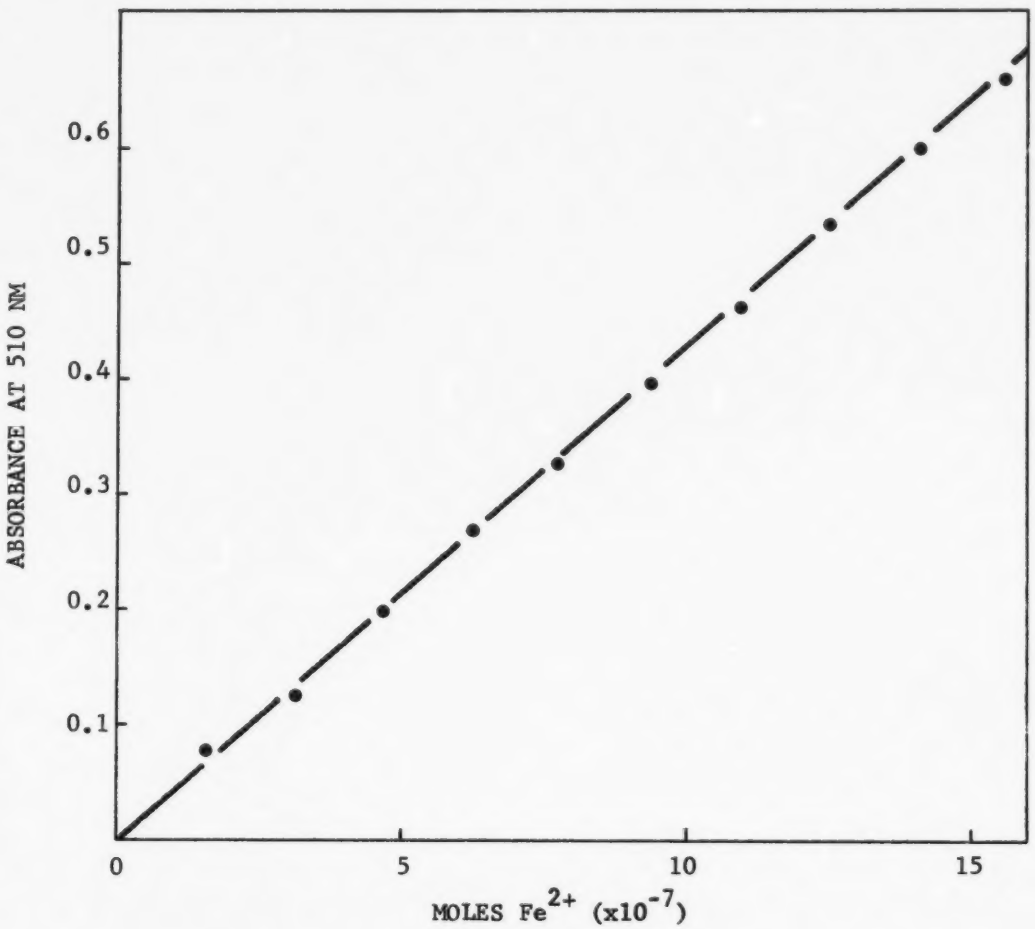

Figure 14. Calibration curve for the analysis of the actinometer solution.

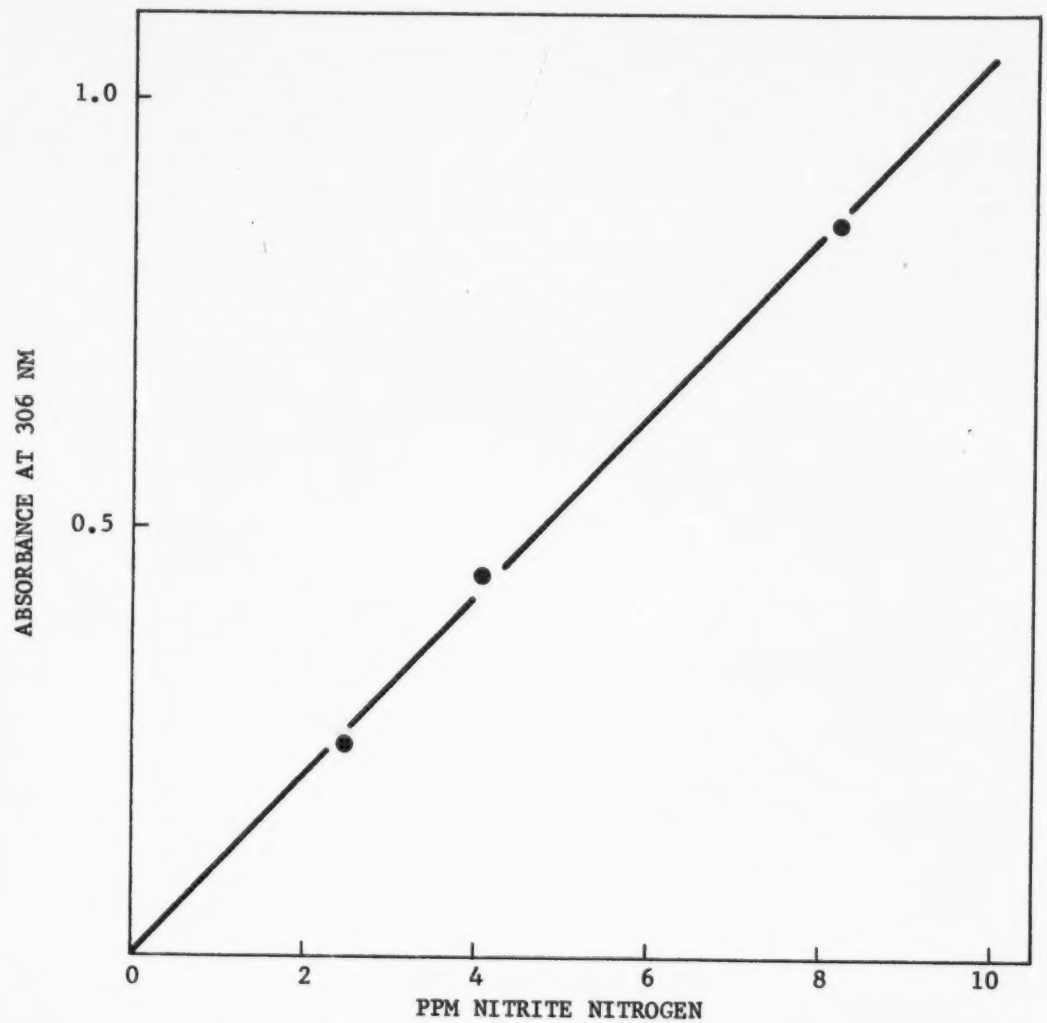

Figure 15. Calibration curve for nitrite analysis.

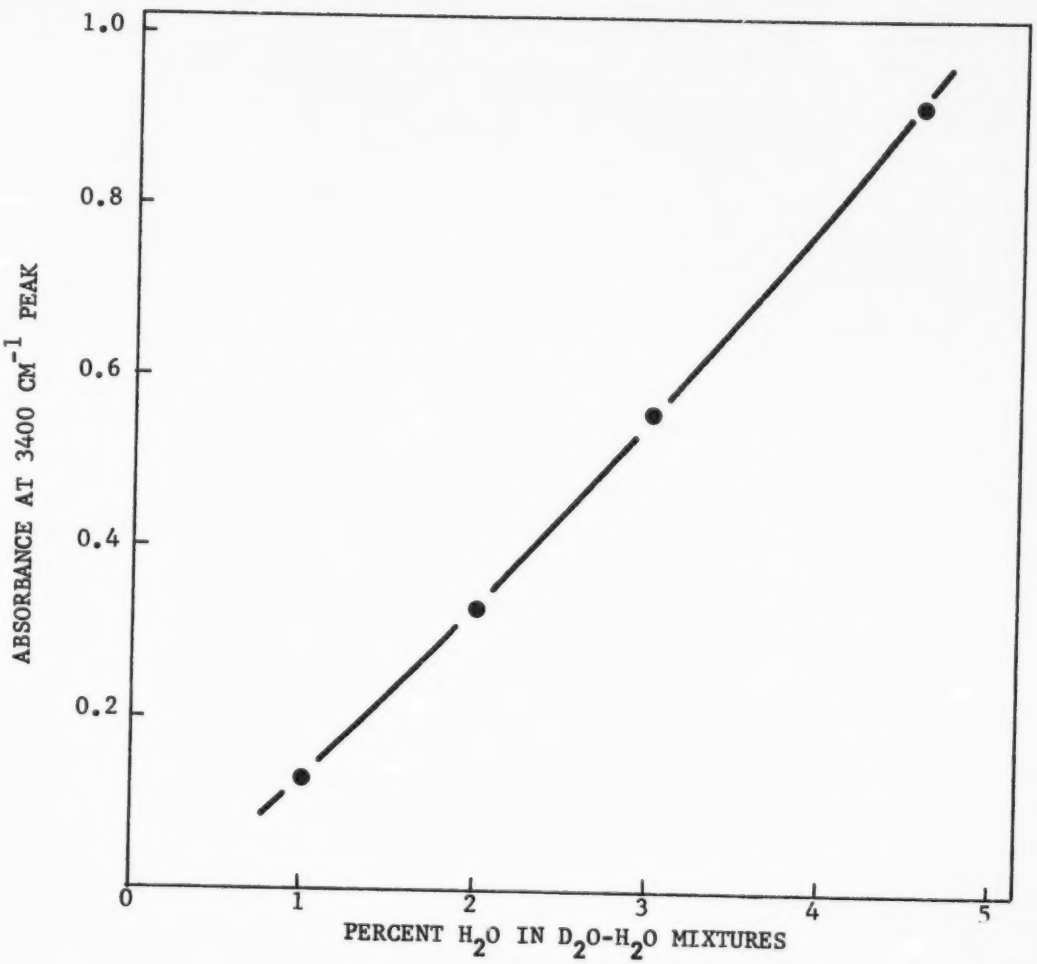

Figure 16. Calibration curve for water accessibility determination.